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THE METALS IN ELECTROCHEMISTRY[1]

By Professor LOUIS KAHLENBERG

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ABOUT two thirds of the chemical elements recognized at present are metals. Of these seven, namely, copper, gold, iron, lead, mercury, silver and tin, have been known since prehistoric times. Antimony and bismuth were discovered by Basil Valentine in 1450; zinc by Paracelsus in 1520; and arsenic by Schroeder in 1694. In the latter half of the eighteenth century ten metals were discovered, namely, chromium 1797, cobalt 1773, manganese 1774, molybdenum 1782, nickel 1751, platinum 1741, tellurium 1782, titanium 1789, tungsten 1781 and uranium 1789. During the nineteenth century about forty-two new metals were discovered. Of these forty-two metals, about twenty-six were reported before 1850, and the remaining sixteen were recognized during the latter half of the century—fourteen of them being isolated before 1890. Radium and lutecium were discovered in the twentieth century.

Thus most of our metals were discovered in the nineteenth century, particularly during the first half of that period, and during the three decades from 1860 to 1890. The reason for this lies mainly in the fact that electrolysis came into use with the electrolytic decomposition of water effected by Nicholson and Carlisle in 1800, and the introduction of practical spectroscopy by Bunsen and Kirchhoff in 1860. Electrolysis and spectroscopy, then, have greatly increased the number of metals (and also other elements) that we now know. Indeed, the finding of another new metal was so common during the nineteenth century that such discoveries almost became monotonous. To be sure new elements have also been found by purely chemical means; that is to say, without electrolysis or spectroscopy. Moreover, the

[1] Presidential address at the meeting of the Electrochemical Society, Birmingham, Alabama, April 24, 1931.

periodic system of the elements as promulgated by Dimitri Mendelejew and Lothar Meyer suggested the existence of new hitherto unknown metals which were very soon found. Furthermore, the discovery of radium in the present century has resulted in finding other elements that are radioactive. In fact the pursuit of radioactivity has rivaled in intensity the efforts directed toward spectroscopy which date back to the latter half of the preceding century.

Now, while the metals are numerous, it is nevertheless true that the atmosphere and the great bulk of the oceans and the lithosphere as we know them are non-metallic, consisting largely of oxygen, hydrogen, nitrogen and silicon, though to be sure the latter has certain metallic qualities. It has been estimated by F. W. Clarke that aluminum, the most abundant metal in the lithosphere, is present to the extent of 7.90 per cent.; and iron which is next in order to the extent of 4.43 per cent.; calcium, magnesium, sodium and potassium forming 3.44, 2.40, 2.43 and 2.45 per cent. of the earth's crust respectively. All other metals and non-metals constitute only a few tenths, and in most cases only a few hundredths, of a per cent. of the earth's crust.

Thus far the metals have played a special rôle in the development of electrochemistry, for they all conduct electricity and they are liberated from their compounds by electrolysis. The latter fact caused Sir Humphry Davy to formulate the first electrochemical theory, which was to the effect that chemical affinity is in reality electrical attraction. Much was made of this view, and the dualistic theory of Berzelius held sway for half a century. In fact, dualism has by no means disappeared from our science. The Arrhenius theory carries with it the essentials of dualism; and, indeed, the present much-heralded hypothesis that all matter is made up of protons and electrons is also dualistic in character. The notion that electricity is material came from the intensive study of Sir Joseph J. Thomson on the discharge of electricity through gases.

Though the idea of the atom dates back to ancient Greece, our present atomic theory, which has held sway for a century and a half, is founded upon the laws of stoichiometry; and our molecular theory has grown out of the law of Gay-Lussac of the combination of gases by volume. So useful have the atomic and molecular conceptions been, and so intensively have they been preached and advocated, that it is almost dangerous to remind people that atoms and molecules are after all only theoretical entities. How many persons actually know that we write the formula of water H_2O instead of HO simply because we want to hold Avogadro's hypothesis? How many actually know that the molecule of hydrogen is written H_2 simply because we want to hold Avogadro's hypothesis? Yet such hypothetical things, valuable though they be, are continually being regarded as actual facts, an attitude which can only retard true progress.

In the nineteenth century the physicists tacitly and even gladly accepted the chemical atoms and molecules founded upon the laws of combination by weight, and by volume in the case of gases. The physicists used the atomic and molecular conceptions in connection with their studies of electricity, heat, light and radiant phenomena with the result that now in the twentieth century they have concluded that the chemical atom is complex and made up of protons and electrons; *i.e.*, electrical particles or corpuscles much smaller than the atoms, whose so-called structure must consequently be studied. The idea that electricity is material in character and that it is the primordial matter out of which our so-called chemical elements are composed has naturally opened up the old question of the transmutation of the elements and particularly the transmutation of the metals. Indeed, observed transmutations have been reported as going on during the process of the decay of radioactive bodies, and thus the old dream of the alchemists has been renewed. While such observations have been reported as going on spontaneously, transmutations effected in the laboratory are lacking. We still get our lead from the Ozarks.

In the study of the metals much has rightfully been made of the fact that the atmosphere surrounding a red-hot metal conducts electricity. The explanation that this is due to electrical particles flying off from the hot metal recalls the old idea of phlogiston, a subtle material which was supposed to leave the metal when it was heated or burned. The phlogistic theory was overthrown by the results obtained by exact experiments with the balance. Nevertheless, this revolution was not accomplished without a hard fight, and it should now be recalled that experimenters of the first order like Cavendish, Scheele and Priestley never relinquished the idea of phlogiston. Now, indeed, what is essentially this same notion is again coming into the foreground under the name of the electronic theory, albeit it is now founded upon an array of experimental data, whereas a hundred and fifty years ago it was largely speculative in character, being based merely upon qualitative observations which were readily discounted in favor of the views of Lavoisier and his followers, who presented exact quantitative data, representing careful weighings, to substantiate their view of combustion.

The balance has had its innings for nearly a century and a half. While the work with the balance was fundamental and important and also inaugurated quantitative experimentation instead of qualitative or quasi-quantitative observations, nevertheless we are now coming to recognize that by no means everything is amenable to study with a balance. In other words, we are gradually emancipating ourselves from the tyranny of the balance. The old romantic spirit of phlogistic times is coming back. It was, indeed, kept alive by the discovery of Dulong and Petit that the heat capacity of the atoms is essentially the same, by Dr. Seebeck's famous discovery of thermo-couples, by Faraday's discovery that chemically equivalent quantities are deposited by the same current, by the thermochemical work of Julius Thomsen and Marcelin Berthelot, by the discovery of Wiedemann and Franz that heat conductance and electrical conductance go hand in hand, by the brilliant work of Bunsen and Kirchhoff on the spectra of the elements, by Crookes' experiments in vacuum tubes, by the x-ray work of Roentgen, and by the radioactive studies of Madam Curie. The fundamental researches of Volta on the contact potentials of the metals and his discovery of how to pile up E.M.F. by connecting batteries in series are specially memorable. They inspired the later work of Kelvin, who measured the potentials of the various metals against his standard gold plate.

For a number of years it has been my privilege to report to this society the results of my researches on the electrochemical series of the metals, the potentials developed by the latter in various electrolytes and the replacing power which the metals exhibit toward one another. Recently the potentials developed by metals laden with gases came into consideration in these researches. All these experiments, and especially the last work on gas electrodes, have convinced me that the effects observed are due principally to the metals and their specific nature, and secondarily due to the electrolytes and gases with which the metals are in contact. This conclusion is in line with the idea expressed by Volta, by Kelvin, and, indeed, even by Nernst when in his theory of contact potential he endows the metals with a specific so-called solution tension.

Theoretically, it should be possible to deposit electrolytically any and all of the chemical elements; there is no limit as to the possibility of forming chemical compounds, both inorganic and organic, by means of the electric current or electric contrivances. In practice, we have developed rather slowly in these matters in recent years. We have been hampered because it has been difficult to find the suitable electrolyte, suitable electrodes, and also the proper conditions of temperature, potentials impressed and current densities to accomplish the purpose in hand. To be sure, in many ways enormous strides have been made in our electrochemical industries. It is not the purpose to rehearse these here. We are plating with chromium now. How to plate with tungsten will be told us at this meeting and perhaps ere long we shall learn how to plate with silicon or even with boron. Yet these are minor details as compared with the great problem of gaining a better understanding of the fundamental nature of the metallic state itself. What is it that gives metals their peculiar and highly specialized character? Why do they conduct electricity? Why are they ductile and malleable and strong in some cases and not in others? Why are they all opaque? Why are they silvery white to steel gray in hue with the sole exceptions of the two colored metals—gold and copper? Why are some of the metals so intensely poisonous to plants and animals and others not? Why are some of the metals so absolutely necessary in considerable quantities in life processes and others not? These and many other questions suggest themselves and must eventually be answered.

The great problem to-day is not to find more new metals, but rather to reduce the present number by showing that they are complex, that they can actually be resolved into something simpler, and that they can be synthesized in actual practice. In this work our present atomic theory, founded as it is upon the weight relations that obtain in chemical combinations, will probably avail us little or nothing. In fact the intensive efforts at unravelling the so-called atomic structure of the elements by means of miniature astronomical models, while interesting, are entirely too significant and do not suggest how to proceed experimentally to accomplish the proposed task. New and novel experimental methods of inquiry must be found. This is the order of the day. Are we of the twentieth century to sit by and try to solve our problems at the writing desk by means of models and equations which start from fixed assumptions and preconceived notions that have ever been recognized as the chief bar to scientific progress? Or are we to go into the laboratory and workshop unhampered mentally and once more guided by the inspiration of the spirit of the great experimental geniuses of the past, using the far superior experimental means at our command, seek to find entirely new and novel ways of approaching the problem of the riddle of the metals? Once this is solved, it will doubtless carry with it the solution of many other fundamental questions. One who continually works with the metals in the chemical and physical laboratories can hardly divest himself of the idea that there is something fundamental which the metals have in common that has thus far entirely escaped us.

The most promising line of experimentation before us at the present time seems to lie in the study of the phenomena in high vacua, in the photoelectric investigations, in the systematic inquiry into thermo-electric and radioelectric effects, and in alternating current rectifiers. Naturally great experimental difficulties are encountered in inquiries of this kind and these are augmented by the inordinate desire to gain premature theoretical conceptions, especially mechanical conceptions of what takes place, when the phenomena in question are probably not at all amenable to explanations of this nature. We must learn to work by faith and inspiration. We must learn again to divine the truth. We must be led as such geniuses as Davy and Faraday were led in their experimental inquiries. What guided them in their fundamental discoveries was a species of intuition, and not complex mechanical theoretical conceptions made still more obstruse by intricate, yet nevertheless quite inadequate, mathematical equations and expressions. Theories have their place. They are useful but they must not be taken too seriously. They must not be believed too hard lest they enslave us and bind us to earth. It is highly desirable to keep the minds and spirits of our younger generation free and unhampered by too serious consideration of theoretical conceptions with which present-day scientific literature overabounds. Rather a jovial, happy-go-lucky spirit of experimentation is to be cultivated, for as the great poet Goethe has put it—"Grau teurer Freund ist alle Theorie und grün des Lebens goldener Baum."

In this spirit and in this sense our efforts toward opening new avenues of inquiry by stimulating novel ways of experimentation that are calculated to reveal undreamt of vistas, our society has established its new division of electronics and paralleled the same with electrothermics and electro-deposition. May this new field prove specially fruitful, may it provoke thought and discussion and yield experimental results of a basal character that shall call for additional, novel divisions of our society so that the ends for which it was founded may truly be realized.

SOME REMARKS ON MATHEMATICAL STATISTICS[1]

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IN casting about for a favorite topic on which to address you on this occasion, I was anxious to give much weight to your feelings as to what would be most appropriate considering both your interests and my limitations. It seemed fairly obvious that you would wish me to speak on a subject of which I have some special knowledge and to which I have made at least a few contributions. These conditions determined the general field in which to select a topic. In spite of these great limitations I wrote down a dozen or more specific topics, but finally selected a subject so broad that it leaves plenty of room for suitable limitations as we proceed. In this way it has come about that I am to make some remarks on mathematical statistics. Although much that I shall say may be an old story to many of you, I shall find something of a child's delight in "saying it again" if I can say it in such a manner as to interest you.

The statistician engaged in the collection of data has sometimes been pictured, like Sam Johnson's maker of dictionaries, as the slave of science doomed only to gather together the material with which others build and press forward to conquest and glory. While this picture may portray a modicum of truth, my experience of over twenty years in the examination of data obtained from a great variety of sources leads me to think that the genuine collector of material ordinarily enjoys the process of collecting more than he would enjoy the more difficult thinking involved in the analysis and interpretation of the data. The analysis of available data often lags far behind the process of collection, particularly in cases of organized research. It is in the process of analysis that mathematical statistics has become, to a very considerable extent, the servant of science.

The publication of the "Théorie Analytique des Probabilités" of Laplace in 1812 marked the culmination of the first great period of activity in the development of the principles underlying mathematical statistics. In fact, the publication of this monumental work of Laplace practically closed the first great epoch of the development of these principles; for, following this publication, relatively few outstanding results or central theorems of mathematical statistics were contributed until our current period of activity which started in the decade 1890 to 1900, with the development of generalized frequency curves and a theory of correlation. To be sure the DeMoivre-Laplace law of error was developed by Gauss and given its important place in the adjustment of observations, but there was, on the whole, relatively little progress.

The activity of the decade 1890 to 1900 may be properly regarded as the inauguration of the second great epoch in the development of mathematical statistics. As early as 1895 the fact had become

[1] Presidential address before the Iowa Academy of Science, May 1, 1931.