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THE RELATIONSHIP BETWEEN ELECTRICAL POTENTIALS AND CHEMICAL REACTIVITY[1]

By Professor LOUIS KAHLENBERG

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We are to-day celebrating the seventy-eighth anniversary of the birth of Edgar Fahs Smith, who was so personally beloved by us all. It is consequently fitting that we pause to dwell upon those phases of our science in which he was specially interested. Though Dr. Smith busied himself with a large number of chemical problems covering a wide field, yet it will commonly be conceded that no work was more dear to him than his electrochemical researches and his studies in the history of the development of chemistry. It would, therefore, seem specially appropriate to consider a topic in these domains, and so I have chosen to invite your attention to the relationship between electrical potentials and chemical reactivity.

The most striking thing about chemical phenomena is the fact that they depend mainly upon the specific nature of the substances that are brought together. Unless the right substances are chosen, no chemical change takes place, no matter what are the conditions of temperature, pressure, concentration or excitations caused by electricity, light or other agencies. The explanation of chemical change has always been the assumption of a specific attraction, that is, an affinity of the substances for one another, an affinity which depends entirely upon the specific nature of the substance studied. Naturally, the desire to measure the intensity of this affinity has occupied chemists quite early in the history of the development of our science. Perhaps the first systematic attempt in this direction was made in the eighteenth century by Torbern Berg-

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[1] Edgar Fahs Smith memorial address delivered at the Chemical Laboratory of the University of Pennsylvania.

man, when he arranged the metals in a series in the order in which they will replace one another in solutions of their salts in water. His work constitutes an important contribution to this day.

As soon as the discovery was made that many substances may readily be decomposed by electrolysis, Sir Humphry Davy, with an impetuosity that was characteristic of him, jumped to the conclusion that chemical affinity is electrical in character and that the constituents of a chemical compound are held together by electrical attraction. He consequently proposed to use electrical means to measure chemical affinity, and developed this idea especially in his Bakerian lecture in 1826.[2] Unfortunately, knowledge of electrical phenomena had not yet progressed far enough to distinguish between what we now call voltage and amperage, and, of course, electrical measuring instruments were in their infancy. As long as attempts were made to use a galvanometer to evaluate chemical affinity, the results were doomed to failure. Davy was a brilliant experimentalist and not a propagandist, and so while he was the first to put forth an electrochemical theory, that fact is usually overlooked. It was through the electrochemical explanations of Berzelius that the dualistic view of chemical combination became thoroughly rooted; for Berzelius was not only a careful and indefatigable experimenter, but he was also a prolific writer. His Lehrbuch and his Jahresbericht were regarded as authority for nearly half a century. Nevertheless, during all this time quantitative relations between chemical affinity and electrical phenomena were not found, for clarity concerning the latter did not yet exist. This is especially emphasized by the fact that Berzelius himself was completely ignorant of the difference between electric current and electromotive force; and so, when Faraday published his laws of electrolysis and cited his experimental facts supporting these laws, Berzelius in reviewing this fundamental work in his Jahresbericht adopted an extremely critical attitude toward it. The views expressed by Berzelius clearly indicated that he did not know the difference between electrical energy, voltage and amperage. This is not at all surprising, for these distinctions were also unknown to Faraday at the time; in fact, they were developed much later.

Faraday worked experimentally. He kept his mind singularly free from preconceived notions—theories which by their implications constitute a serious hindrance to the discovery of new, fundamental facts. His efforts to unravel the nature of electrical conductance, especially when it is accompanied by chemical decomposition, namely, electrolysis, are a masterpiece, albeit he did not succeed in solving the mystery, and we still find ourselves at the present day without adequate explanations to account for the many facts that we possess.

When in the forties and fifties of the nineteenth century, through the efforts of Julius Robert Mayer, Kelvin, Helmholtz, Joule and Clausius, the mechanical theory of heat was developed and our notions of the transformation of energy became clarified, and Kelvin actually computed the E.M.F. of the Daniel cell from a knowledge of Faraday's law and the heat of the chemical reaction, $Zn + CuSO_4$ aq. $= ZnSO_4$ aq. $+ Cu$, and found that the result agreed with the experimentally determined voltage of the cell, a very important advance had been made. The attempt to apply the same methods to the Latimer Clark cell containing mercury and mercurous sulphate, instead of copper and copper sulphate, as in the Daniel cell, at first failed and cast a gloom on the situation; but Helmholtz pointed out that the discrepancy between computed and found value was due to the fact that the Clark cell has a high temperature coefficient, as compared with the Daniel cell, whose temperature coefficient is so low as to be practically negligible. He developed his famous equation in which the temperature coefficient is duly considered, and this cleared away the existing difficulties.

As a consequence of this recognition of the fundamental facts of the transformation of energy and of the development of the means of measuring energy and its intensity and capacity factors, ideas were clarified and the road to substantial advancement was opened.

The period of 1850 to about 1880 was notable for the development of thermal chemistry. The dominant idea during these three decades was that chemical affinity could be evaluated by measuring the heat evolved or absorbed during the reaction in question. Both Julius Thomsen and Marcellin Berthelot practically devoted their lives to the attempt to measure chemical affinity by thermal means. In their enthusiasm, industry and zeal, they invented and perfected many calorimeters to accomplish their purpose. They determined in the laboratory and finally compiled an enormous amount of thermochemical data which form a valuable stock of knowledge. They also formulated generalizations in the shape of laws governing these thermochemical phenomena. Nevertheless, the main objective, namely, the evaluation of chemical affinity, was not achieved, for the reason that the thermal accompaniment of a chemical change represents the algebraic sum of a number of processes, physical and chemical, that take place during the reaction, and it is commonly not possible to evaluate each of these separately as to its effect on the final heat change that is actually measured. The realization of this

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[2] *Philos. Trans.*, p. iii, 1826, and *Phil. Mag.*, 1, 31, 1827.

came after most of the thermochemical experiments had been done. Perhaps the most promising thermal measurements for comparing chemical affinity are the study of the avidity of acids by Julius Thomsen; but even here the conclusions reached are subject to question in the light of more recent experimentation.

The resurrection of the law of mass action by Guldberg and Waage in the sixties of the last century gave an impetus to the study of the speed of chemical change and chemical equilibria. This enabled the logical arrangement of acids and bases, according to their relative affinities; and to the present, the law of mass action, and its consequences, offers the best means we have of comparing chemical affinities, so that investigations of the rate of chemical change and of chemical equilibria are justly popular.

With the advent of Arrhenius' hypothesis in the eighties, attention was again centered on electrochemical matters, and the idea gradually grew that electrolytic conductance and chemical reactivity go hand in hand, so that, for example, the strength of an acid or a base could be compared by the electric conductance of its aqueous solutions. This theory naturally spurred experimental inquiry in the study of the electric conductance of aqueous solutions. It was closely followed by Nernst's theory of the electric potential developed by a metal when it dips into a solution of one of its salts. This hypothesis, which one might be disposed to term a natural consequence of Arrhenius' theory and van't Hoff's view of solutions, led to many experimental determinations of so-called single potentials of the various metals in solutions of their own salts, from which data the theoretically conceived "solution tensions" of the several metals were then computed. These solution tensions were generally expressed in atmospheres, and they were either fabulously large or ridiculously small, varying, for example, from about 9.9×10^{18} atmospheres for zinc to 2.3×10^{-17} atmospheres for silver, the logarithmic nature of the Nernst function resulting in these fantastic figures, which are still paraded in good faith in many of our text-books.

Quite aside from Nernst's rather mechanical theory, the idea that chemical energy can be transformed into electrical energy and that the intensity factor of electrical energy, namely, the electric potential, is proportional to the intensity factor of chemical energy, namely, chemical affinity, appears thoroughly sound; and since in all cases of electrolytic decomposition Faraday's law holds, it should be quite possible to compare chemical affinity by the method of Kelvin and Helmholtz from the voltages developed.

Nernst's theory inspired much experimental work, though this was actually directed toward determining electrode potentials of the metals in dilute aqueous solutions of their salts, and not at all toward ascertaining the real cause of such potentials, for the theory itself already stated that as known.

The arrangement of the metals in a series, according to their electrode potentials, is commonly known as the electrochemical series of the metals, and such a series is in general parallel to that obtained when the metals are arranged according to their chemical replacing power. Nevertheless, the two are by no means always identical.

For a number of years I have studied the electrochemical series of the metals in the laboratory, and it has been found that the series is a function of the solvent and of the substance or substances dissolved in the latter as well as of the specific nature of the metal of which the electrode consists. These researches have appeared in the *Journal of Physical Chemistry* and the *Transactions* of the American Electrochemical Society. In these papers it has been demonstrated that the electrochemical series of the metals is not a fixed thing.

It is particularly interesting that the brittle metals, like arsenic, antimony and bismuth, and even silicon, which are frequently called half metals or metalloids, lie higher in the chemical series than do many of the real ductile and malleable metals like copper, silver, gold and platinum. As a striking illustration, the slightly basic power of arsenic will be commonly admitted, for it unusually functions as a part of the acid radical in its salts; and yet, arsenic lies relatively high in the electrochemical series. It readily replaces copper, mercury, silver, gold and platinum from aqueous solutions of their salts. The electrode potentials of arsenic in these cases run parallel with the replacing power. One is specially surprised that silicon should also be able to replace copper and that its potential lies above that of the latter. Silicon is usually regarded as less metallic than arsenic.

For many years the Royal Society of London had a committee on the seat of E.M.F. of the voltaic cell. At this time, Kelvin performed his interesting series of experiments in which he measured the potentials which the various metals developed against a gold plate used as a standard. In the course of those investigations, it was shown that the potential of a metal is determined primarily by its specific nature, but that it is nevertheless very materially influenced by the mechanical treatment to which its surface had been subjected. So, for instance, the potential of zinc taken from a cast piece may be raised successively by scratch-brushing it, polishing it and finally burnishing it on a steel burnisher. On the other hand, the electrode potential of zinc in aqueous solutions is not much altered by such treatment, which might well call into question whether the contact potential and the electrode potential are, after all, quite comparable.

In Chapter 12 of his book, "Electrochemie, Ihre Geschichte und Lehre" (1896), Wilhelm Ostwald relates and critically reviews the controversy between the contactists (*i.e.,* the followers of Volta who insist that E.M.F. is developed by mere contact of two different bodies) and those who contend that E.M.F. is due to chemical forces. Ostwald unquestionably exerted himself to present both sides of the problem impartially; nevertheless, being at the time personally enamored of the Arrhenius and Nernst theories, he was quite unable to divest himself of the effects of these doctrines.

It has now been definitely established experimentally that, whenever two different bodies touch each other, an electrical disturbance takes place and both bodies become oppositely charged. This is true in all cases, no matter whether the bodies be solids, liquids or gases. The charges developed depend as to sign and intensity on the specific nature of the bodies that are brought together. Moreover, two bodies that are chemically identical and more or less different physically will also develop differences of electrical potential when brought into contact. Those who contend that E.M.F. is caused by chemical action insist that only thus can one understand where the electric energy comes from, and they have in their favor the fact that demonstrable chemical action does accompany electrical potentials in many cases. On the other hand, it can not be questioned that potentials are also developed when there is no chemical action. Ostwald (*loc. cit.*) points out that Pfaff, one of the great exponents of the contact view of Volta, finally sought to show that the contact view and the chemical theory do not necessarily mutually exclude each other. His explanation was highly regarded by his contemporaries, particularly by Faraday and Schönbein. What the notion amounts to is that gross matter is enveloped by an electric atmosphere, which is clearly defined yet different around different bodies, and which is disturbed whenever the latter touch each other, thus bringing about differences of potential. With our present electronic theory of matter, the views of the contactists and chemical contenders are, of course, far more readily harmonized; for it can easily be understood that electrical strains can be set up between two bodies that are in contact, before they actually react chemically upon each other so that this can be experimentally detected.

Perhaps no phase of the study of electromotive forces is of greater interest than that of the so-called gas electrodes. I have in mind especially the hydrogen electrode. Gas electrodes[3] have really been known ever since the electrolysis of water was discovered. A gas electrode consists of a metal or some other first-class conductor in which the gas in question is absorbed, this electrode dipping into an electrolyte. Through the Nernst theory the potential of such electrodes became a special object of study. This is particularly true of the hydrogen electrode, by means of which the so-called hydrogen-ion concentration of a solution, that is, its degree of acidity or alkalinity, may be measured.

The term gas electrode is really a misnomer, for the gas electrode is in fact a gas-metal electrode or a gas-carbon electrode, the first-class conductor in which the gas is adsorbed having a perfectly distinct and definite effect upon the potential that is developed. At the same time, it is not to be denied that the gas also powerfully affects this potential. The hydrogen electrode is usually formed by absorbing that gas in an electrode of platinized platinum, and such electrodes, though they are platinum-hydrogen electrodes and not merely hydrogen electrodes, are fairly reproducible experimentally. Moreover, they serve well to indicate different degrees of acidity, as is well known. This, according to the Nernst theory, is to be ascribed to the fact that equilibrium between the hydrogen of the electrode and the "hydrogen ion" in the electrolyte tries to establish itself, and hence the hydrogen electrode "reacts" on "hydrogen ions" present. However, it has recently been demonstrated[4] that quite a number of other electrodes which are not at all laden with hydrogen indicate the acidity or alkalinity of solutions quite as well and even better than the so-called hydrogen electrode. Among these electrodes plain tungsten and molybdenum occupy a foremost place. This observation has manifestly nothing to do with Nernst's theory, the inadequacy of which I have pointed out thirty-three years ago. In fact, electric titrations of acids and bases by means of a tungsten electrode are more readily effected and more convenient than by means of a so-called hydrogen electrode. Just why metals like molybdenum, tungsten and antimony should be sensitive electrical indicators toward acids and bases is not yet fully understood. Other metals, like copper and silver, are not at all sensitive in this respect, and so the tungsten-copper or the tungsten-silver couple may be used to ascertain the degree of acidity of solutions. All that is necessary is to dip such a couple into the solution in question and measure the E.M.F. developed, which is a known function of the acidity. The polarity of such couples actually reverses after passing the point of neutrality, showing that the combination is unusually sensitive. Moreover, tungsten develops and maintains

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[3] See *Trans. Amer. Electrochem. Soc.,* 58, 107, 1930.

[4] *Trans. Amer. Electrochem. Soc.,* 56, 201, 1929, and 57, 361, 1930.

its own potential so strongly that it is but slightly affected by the presence of gases. That is to say, a tungsten electrode, loaded with hydrogen or any other gas, develops about the same potential in all cases. *This is a specific property of tungsten.* Molybdenum acts similarly; that is to say, both of these metals are very sensitive to changes in the degree of acidity or alkalinity of a solution. The electrical sensitivity of the various metals toward acidity and alkalinity has been carefully studied in my laboratory, and the order of the metals in this respect is about as follows, the most sensitive being given first: Pt (platinized), W, Sb, Mo, Pt (plain), As, Si, Bi, C (Acheson graphite), Cr, Au, Cu, Ag, Pb, Fe, C (natural graphite), Cd, Ni, Co. It is evident from this that the order has nothing to do with the electrochemical series or with the periodic system. It stands alone, and one can not at present connect this property with any other known property of the metals concerned. Thus the series is a singular one, just as is the case with the thermoelectric series of the metals. Further experimental inquiry will probably yield an explanation of this curious property of the metals.

When arranged as to their sensitivity toward gases, as determined by the single potentials which they develop, the order of the metals is about as follows, the metals whose potential is most affected by gases being given first: Pt, Ag, Cr, Cu, Fe, Mg, Sn, As, Au, C, Cd, Pb, Hg, Mo, W, Zn.

Here again we see no relationship to the periodic system nor to any other known property of the metals concerned.

The systematic investigation of gas electrodes, so-called, in my laboratory has shown that metals whose single potential is altered by any one gas, like hydrogen, for example, are also marked affected by other gases, like oxygen, nitrogen, helium, argon, neon, carbon monoxide, methane, ethylene, acetylene, etc.

When I first reported my experimental work on nitrogen electrodes at a meeting of chemists at Chicago, I was told that nitrogen electrodes can not exist, since there are no nitrogen ions known. I naturally remarked that that did not bother me at all. One can see from this incident, however, the unfortunate influence of the Nernst theory in thwarting experimental inquiry by virtue of its implications. Nitrogen electrodes are quite as active as hydrogen or oxygen electrodes. In fact the same is true of electrodes of compound gases and even of electrodes of the noble gases, argon, helium and neon. The following Table I gives the potentials of the elemental gases when these are adsorbed in platinized platinum and immersed in nKCl, nKOH, and nHCl solutions, respectively. The figures represent millivolts and are then in each case the total E.M.F. of the electrode in question against the usual nKCl calomel electrode.

TABLE I

PLATINUM, PLATINIZED ELECTRODE POTENTIALS[5]

	nKCl	nKOH	nHCl
Nitrogen	–330	106	517
	–332	101	512
Hydrogen	398	817	301
	399	815	298
Argon	359	1,050	305
	360	1,039	303
Helium	295	1,012	102
	296	1,010	98
Oxygen	357	28	–6
	360	23	2
H_2 and O_2	755	789	307
Chain	759	789	296
H_2 and N_2	728	711	–216
Chain	731	714	–214
N_2 and O_2	27	78	523
Chain	28	78	510
H_2 and He	103	–195	199
Chain	103	–195	200
He and O_2	652	984	108
Chain	656	987	96
N_2 and He	–625	–906	415
Chain	–628	–909	414
H_2 and A	39	–233	–4
Chain	39	–224	–5
A and O_2	716	1,022	311
Chain	720	1,016	301
A and N_2	689	944	–212
Chain	692	933	–208
A and He	64	38	203
Chain	64	29	205

Table II gives similar data in volts obtained with plain platinum electrodes of the compound gases.

TABLE II

PLAIN PLATINUM GAS ELECTRODE POTENTIALS

	O_2	CO	C_2H_2	C_2H_4	C_2H_6	CH_4	H_2
nKOH	0.213	0.245	0.264	0.280	0.318	0.337	0.348
nKCl	–0.004	0.013	0.024	–0.002	0.061	0.038	0.119
nHCl	–0.342	–0.232	–0.210	–0.202	–0.191	–0.184	–0.176

An inspection of Table I clearly shows that nitrogen and the noble gases give fully as high and as individually characteristic potentials as do hydrogen and oxygen. All work was done at room temperature 20° C. Neon has also been found to develop similar characteristic potentials of its own. The results will soon be published.

In the case of the compound gases studied, Table

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[5] The two values given in each case were obtained from independent experiments and consequently indicate how closely the electrodes are reproducible.

II, it is evident that the potential developed varies regularly with the composition of the gas from acetylene, which contains least hydrogen, to methane, which contains most.

In all gas electrodes the results are greatly affected by the nature of the first-class conductor in which the gas is absorbed. Table III[6] gives an interesting arrangement of the elemental gases. It represents these in decreasing order of the basicity of the potentials which they produce in three different electrolytes and when absorbed in the various metals listed.

Regarding these experimental data, particularly the potentials developed by helium and argon, which are chemically inert and so far as we know at present do not form chemical compounds at all, one naturally again raises the question, Are the potentials developed by mere contact or are they due to chemical action? It is quite certain that one can not say, at least so far as the noble gases are concerned, that the E.M.F. is due to chemical action, for no chemical change takes place, and we know of no authenticated cases in which these gases have gone into chemical combinations. One might, however, argue that the potentials are, after all, caused by chemical affinity, that is, by special chemical strains, which are insufficient in magnitude to overcome existing cohesions and are consequently unable to produce actual chemical reactions. The data collected in the case of the noble gases might, of course, be construed as indicating that those gases are by no means as inert chemically as is at present supposed, and that special exertions ought once more to be made to form chemical compounds with them and other elements. Such experimentation would doubtless be desirable, especially since recently some biologists have reported that life can not endure in an atmosphere composed of pure oxygen and nitrogen, thus indicating the possibility that the rare gases of our atmosphere might after all play an important rôle, and that it may be chemical in character.

Instead of using the observed potentials of the rare gases as an argument in favor of the contact theory and against the chemical development of potential, I am disposed to use those facts rather as an indication that we are still quite ignorant as to the real fundamental relation between what we term gross matter, on the one hand, and electricity, on the other. To be sure we are now, on the basis of our electronic theory of matter, constructing quasi-astronomical configurations to represent each of the atoms of the known chemical elements; and I have no fault to find with this, for I am still in hopes that this atomic structure speculation may lead us to some new knowledge and not prove to be merely another interesting attempt to account for some of the facts we have observed. It is well to bear in mind that our conception of a chemical element is that of a substance which has thus far defied our efforts to resolve it into something else, and that our atomic theory is founded on the ratios in which the elements combine by weight, that is to say, upon the three stoichiometric laws. Moreover, it is also well to recall here that the molecular conception has for its basis the laws of Gay Lussac of combination of gases by volume and that, for instance, we distinguish between the atom H and the supposed molecule H_2 simply because we want to hold Avogadro's hypothesis, which naturally grows out of the facts of Gay Lussac's law, when it is regarded in the light of the atomic theory. This being the real situation, is it surprising that we are not able to correlate optical, electrical, radiant and kindred phenomena with our atomic conceptions; and that, however valiantly pursued, our so-called atomic structure ideas are not yielding what they at first promised?

This is preeminently a time when careful, entirely new experimentation is necessary—experimentation that is not overawed by the work of the desk warriors, who with long intricate mathematical equations founded upon inadequate factual data overawe the young, ardent experimenter and stifle his efforts by leading him to think that practically everything of a fundamental nature is already ascertained, and that only a few little finishing touches are now required to complete the picture.

To the young investigator I would rather say—and I am sure that in doing so I would voice the spirit in which Edgar Fahs Smith ever worked and taught and inspired his students—Go into the laboratory and by means of careful experimental inquiry and observation seek to unravel the problems of our science, seek to penetrate the mystery of the relation between gross matter and electricity and thus solve the relationship between chemical reactivity and electrical potentials.

OBITUARY

ULYSSES SHERMAN GRANT

DR. ULYSSES SHERMAN GRANT, professor and head of the department of geology and geography at Northwestern University, died at Evanston on September 21. The end came unexpectedly after a brief illness and a major operation, following his return from the

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[6] This rather elaborate table, giving the results with twenty-nine different metals, each laden with A, H_2, He, O_2 and N_2, respectively, and investigated in KCl, KOH and HCl, is identical with that on p. 143, Vol. lviii, *Trans. Amer. Electrochem. Soc.*, and so is not reproduced here.