

ON THE INFLUENCES CONTRIBUTING TO THE VARIATION
OF CONTACT ELECTROMOTIVE FORCE WITH TIME.¹

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IF a freshly cut zinc surface is placed in a vacuum opposite a copper plate and light of frequency ν is allowed to fall on the zinc surface, the electrons thus emitted will leave the plate with energy

$$\frac{1}{2}mv^2 = h\nu - \omega,$$

where h is the Planck constant and ω a constant peculiar to the metal. Richardson² has identified ω with the work done by an electron, starting from the interior, in crossing the surface of the conductor. Using a statistical method and thermodynamical arguments he obtains the relation

$$V - V' = \frac{I}{e} \left\{ \omega - \omega' + R\theta \log \frac{n'}{n} \right\},$$

where $(v - v')$ represents the contact difference of potential between the two metals in terms of the difference between the work done by an electron in crossing the boundaries of the respective metals, plus an expression representing the Peltier effect. This last term is small compared to the contact difference of potential and will be neglected. This interpretation has found support through the experiments of Richardson,³ Compton, Cooke, Wilson and others.

A second interpretation of the constant ω has recently been adopted by Millikan.⁴ His view point is taken from the interior of the metal. He assumes ω to represent the sum of two independent quantities p_1 and p_2 . Where p_1 represents the work necessary to just separate the electron from the atom, and p_2 the work necessary to separate it from the metal so that an accelerating field can remove it.

Using this conception we may define the contact difference of potential as

$$V - V' = \frac{p_2 - p_2'}{e}.$$

¹ An abstract of this paper was presented before the Am. Phys. Soc., April 21, 1916.

² Richardson, *Electron Theory of Matter*, p. 455.

³ See Richardson's *Electron Theory of Matter*.

⁴ Millikan, *PHYS. REV.*, 7, p. 27, 1916.

If we now let ν_0 and ν_0' represent the frequencies of the long wave-length limits at which the photoelectric action of the two metals under comparison just ceases, we may write for the values of ω and ω' in Richardson's equation the values

$$\begin{aligned}\omega &= h\nu_0 = p_1 + p_2, \\ \omega' &= h\nu_0' = p_1' + p_2',\end{aligned}$$

which in connection with the above definition gives us Millikan's equation for the C.D.P. in terms of Einstein's equation,

$$V - V' = \frac{1}{e}(h\nu_0 - p_1) - (h\nu_0' - p_1').$$

A conception of the contact difference of potential between two metals, in terms of the difference between the amount of energy removed from the incident beam of light and the energy of separation of the electron from the atom. Millikan's results show a very close agreement with his theory, in some cases the difference between the C.D.P. measured directly and that computed from a simplified form of the above equation check within one per cent. This evidence more than any other gives us a direct proof of an intrinsic contact difference of potential other than that induced by exterior or interior chemical effects.¹

A somewhat similar argument, though not involving the definition of C.D.P. as given by Millikan, was published by Einstein.² He assumed the existence of a "double layer" at the metal-dielectric boundary, which gave rise to the C.D.P. It was situated so that its negative surface was always away from the metal. Experimental evidence for the existence of such a double layer may be found in the recent literature dealing with the photoelectric effect.³ An electron, Einstein concludes, in leaving the metal can only do this if it overcomes the potential gradient V existing in the double layer. The energy eV to do this is only attained when the frequency of the incident light has a value given by

$$eV = h\nu.$$

In a similar way a second metal possessing a double layer of gradient V' can only lose an electron through a frequency ν' . Hence

$$V' - V = \frac{h}{e}(\nu' - \nu)$$

represents the equivalence of this contact difference of potential. This

¹ For a summary of the arguments "Chemical C.D.P. versus Physical C.D.P." see Oliver Lodge, *Phil. Mag.*, XLIX (1900).

² *Ann. d. Phys.*, 20, p. 203 (1906).

³ Stuhlmann and Compton, *PHYS. REV.*, 2, p. 199 (1913). Seeliger, *Phys. Zeit.*, XIV., p. 1273 (1913). Compton and Ross, *PHYS. REV.*, 6, p. 207 (1915).

relation, like that of Millikan's, shows that the red wave-length limit of the incident light producing photoelectrons, moves towards the region of smaller frequencies as the contact difference of potential between the two metals increases towards positive values. This important point will be reconsidered when we investigate the data showing the effect of the accumulation of gaseous layers of variable concentration on the surfaces of metals and their influence on the C.D.P.

A final, though none the less important, point of view must be considered, namely that obtained when investigating the C.D.P. from without the metal. This group of literature, since Lodge's classical summary, is unique in its seeming contradictions. In a general way the data dealing with the causes of the variation of C.D.P. may however be divided into two groups.

First that group of investigations which show that the C.D.P. will gradually increase with time. The equilibrium value resulting in a greater electronegative or electropositive value, depending on the method used in cleaning the surfaces under investigation. Their gradual change to a steady value has been definitely observed by Shaw.¹ He attributes this change to the presence of charged surface layers. The rate of charging or removal of layers responsible for the C.D.P. is shown to be independent of the metal and identical with the behavior of ordinary charges imparted by external means. More recently Compton² had determined an empirical relation between C.D.P. and time in the form of an exponential equation. To attribute such a change to a local chemical action seems improbable from the data submitted.

Second that group which has observed fluctuations of the contact electromotive force in the presence of gases to such an extent that no positive conclusions can be drawn concerning the seat of the electromotive force. Such seemingly inconsistent results were usually attributed to "insoaked air films" on the surface of the metal. Spiers³ also has shown that films of hydrogen on the surfaces of the metals tend to move their C.D.P. to more electronegative values, while air films tend to make them more positive. That temporary high potentials are attained when a metal is burnished, that no two methods of cleaning a surface produces the same value of the C.D.P. and that all experiments show fluctuations of the potential with time, with no tendency for the voltage to settle to a final steady value.

The most important advance seems however to have been made by

¹ Shaw, *Phil. Mag.*, 25, p. 241 (1913).

² Compton, *PHYS. REV.*, VII, p. 212 (1916).

³ Spiers, *Phil. Mag.*, 49, p. 83 (1900). See also Broglie, *C. R.*, 152, p. 696 (1911).

Beil,¹ at the instigation of Hallwachs, who had observed the fluctuations of the contact electromotive force in connection with his photoelectrical work. Beil observed a fatigue of the contact electromotive force of zinc in the presence of water-vapor. He attributed it to the formation of hydrogen on the surface of the metal. This explanation seems to be supported by the experiments of Russel.² The observed decrease in the case of zinc was of the order of magnitude of about .2 volt during the first half hour. In the interior of a closed vessel this decrease was lessened. He also showed that the smaller the vessel the more electro-negative the change and that eventually the change was in an electro-positive direction for very small vessels. This in conjunction with his experiments on the effect of dry and moist air led him to the conclusion that dry air acts like a small vessel changing the C.D.P. to more electro-positive values while moist air acts like a large vessel, producing more electronegative values with time. The action was traced to the influence of water-vapor, or carbon dioxide in the presence of water-vapor and the lessening due to the smaller motion of the air.

The photoelectric aspect, seemingly promising, throws very little if any light on the influences at work which change the contact electromotive force with time. It therefore becomes of interest to attack the causes of the change from a point of view exterior to the metal, with the hope that the seeming contradictory results possess some common underlying generalization.

The measurements to be described in the following pages were made in a copper cylinder, Fig. 1, oxidized to a matte black. No solder was exposed on the inner side and all grease was carefully removed. This produced a stable and dense surface practically incapable of occluding gases. In a previous experiment where it had served as part of a photoelectric cell it had been noted for its constancy of contact electromotive force in photoelectric velocity measurements. The metal under examination was placed coaxial to the cylinder. It was either in the form of a rod, or a thin narrow strip of the material. This was attached to a screw clamp of brass which was insulated from the cylinder by means of a high-grade, hard red sealing wax. The rod led to the electrometer calibrated to read volts (776 div. per volt). All parts of the apparatus except those between which contact electromotive force is measured must be covered with hard sealing wax so as not to influence the results. The only opening in the cylinder was a one-centimeter hole, leading to a molecular pump used to remove the gases as occasion demanded.

¹ Beil, *Ann. d. Phys.*, 31, p. 489 (1910).

² Russel, *Proc. Roy. Soc.*, 63, p. 109 (1898).

Two methods of measurement were reported to and were used as checks where experimental conditions warranted.

The usual method consisted in noting every thirty seconds the increments in potential of the electrometer. Under these operating conditions² the cylinder was maintained at zero potential and the ionization current was supplied by a constant source of gamma rays placed at *S*. As a check to these readings a compensation or null method was used. For this purpose the cylinder was connected to a potentiometer circuit, and the potential adjusted so that no current passed between the cylinder and plate. The applied potential as indicated on a standard Weston voltmeter gave the magnitude of the contact difference of potential under observation. These measurements were made to two one thousandths of a volt.

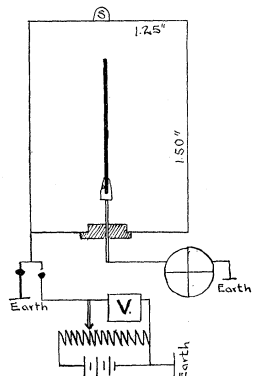


Fig. 1.

Sources of Error.—Owing to the appreciable capacity of the system and intentionally chosen small ionization current, the rate of charging the electrometer is in many instances rather slow. Its readings starting from zero increase exponentially with time, although the contact difference of potential does not possess a zero value, for time equal to zero. The readings therefore will only indicate changes in this exponential charging of the electrometer. It was early discovered that no other sources of contact electromotive force must exist in the circuit containing the metal under observation. Such stray electromotive forces may account for the many and curious variations superimposed upon the normal course of events occurring in the test chamber. It is important that the radium source is so protected that no ionization can take place outside of the restricted volume of the cylinder. The source *S* must also be placed centrally and symmetrically to the metal under examination, so that the ionization may be uniform throughout the volume of the gas.

General Results.—The metals platinum, carbon, palladium, copper and zinc were examined. The first three of this group were chosen for their pronounced property of occluding gases, the last two because of the known investigations of other observers. All data on these metals, arbitrarily as to the history or method of treatment before contact measurements were made, were found capable of classification into two

¹ N. Shaw, loc. cit.

² Kelvin's ionization method, *Phil. Mag.*, 56, p. 82 (1898).

groups. The first group was of the type illustrated by the simple exponential curve in Fig. 2. If no impurity were added to the surface in the form of alcohol, water or oil, all metals investigated in the presence of pure dry air, arbitrarily as to how they were cleaned, produced the simple exponential rise of the electrometer with time. The second group of results possessed characteristic variations due to the presence of water-vapor in the gas surrounding the metal. These variations were often very complex. An initial rise in potential was followed by a corresponding fall or vice versa. Often this double change would lead to a complete reversal in sign of the contact difference of potential. It was found that the results leading to the more complex variations were always due to

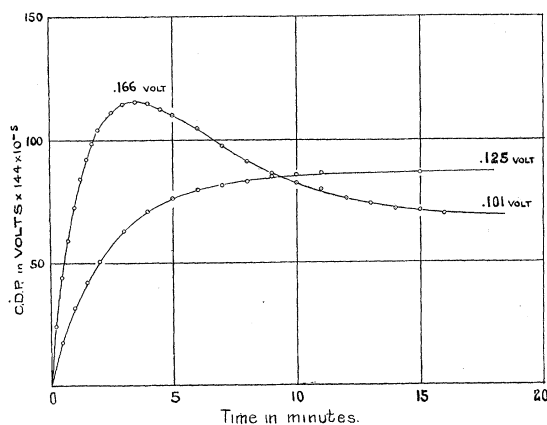


Fig. 2.

some exterior, controllable cause other than that taking place at the surface of the metal. In the final analysis these curves were all reducible to the simple double exponential type shown in Fig. 2.

Variations in the surface conditions, however, change the value of the constants of the pure exponential curve, so that no two treatments of the same metal produce the same equilibrium values. In the presence of water-vapor this was found to be even more pronounced. For instance the difference between the equilibrium values for a burnished and scraped platinum plate examined in the presence of water vapor, not only produced an increase of several tenths of a volt in the end value but also a decrease of two tenths of a volt in the maximum.

Results from Carbon and Dry Hydrogen.—In view of the recent data from the photoelectric effect it is allowable to assert that the contact difference of potential has its origin in the immediate surface and not in the interior of the metal. If therefore a metal is chosen, whose surface

characteristics can be controlled without producing changes such as accompany scraping or polishing, the above results could possibly be more easily analyzed. Now charcoal possesses to a marked degree the property of occluding gases, resulting in changes in the concentration of the gas, forming the surface layer of the material.

In this connection Berger¹ has shown that cocoanut charcoal will absorb as much as 24 c.c. of air per gram of charcoal at 18° C. and 752.9 mm. of pressure. If the carbon is heated to 550° C. and cooled in vacuo, its ability to absorb air increases exponentially with time, which reaches its maximum in about sixty minutes. For different gases the amount absorbed depends largely on the pressure of the gas.

To produce the necessary cocoanut charcoal, of a uniform texture and known previous history; a large and very thick cocoanut shell was broken into large pieces and carbonized in an electric furnace, then cooled with the exclusion of air. The largest pieces were now cut and sandpapered into thin strips, one half centimeter wide, about three centimeters long and one millimeter thick. These strips were placed in the clamp as shown

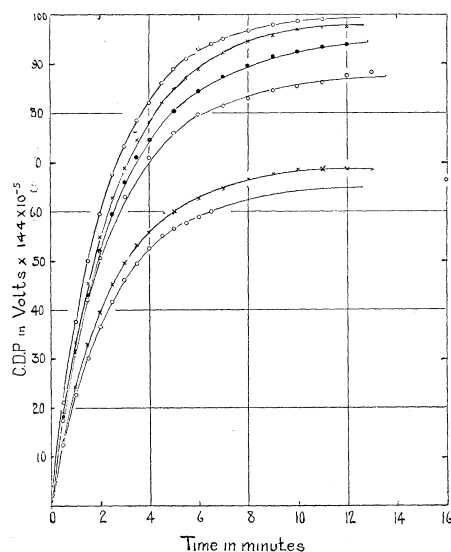


Fig. 3.

in Fig. 1, and connected to the electrometer. The apparatus was evacuated by means of a molecular pump until the pressure was reduced to 10^{-6} cm. or less. Initially the carbon gave off a considerable quantity of gas which upon spectroscopic examination showed complex hydrocarbon bands; this evolution of gas gradually decreases and eventually

¹ F. Berger, *Ann. d. Phys.*, 37, p. 472 (1912).

disappears. Pure dry air is now introduced into the cylinder and allowed to stand for half an hour. This cleaning of the carbon plate was repeated until the gas pumped off was spectroscopically free from gases other than air. The drying took place through a liter Wolf bottle filled with concentrated sulphuric acid, from which the air passed through a thirty-centimeter tube of lump calcium chloride, thence through a three-meter tube of phosphorous pentoxide two centimeters in diameter.

The carbon was now examined for contact electromotive force in this dry air. The resulting charging of the electrometer with the equilibrium value attained is shown in the upper curve of Fig. 3.

If a small amount of dry pure hydrogen, made from chemically pure zinc and sulphuric acid, is now introduced into the cylinder, the hydrogen will be occluded at the expense of the air. The mixture was allowed to stand over night, after which it was assumed equilibrium had been established. The contact electromotive force was then determined. Under these conditions the second curve from the top was generated, the equilibrium value becoming more electropositive by 178×10^{-5} volts. Successive increases in concentration of the hydrogen produced the successive lowering of the equilibrium values, until a point was reached where the absorbed gas was only pure hydrogen, when no further lowering of the end value occurred. The final value was .0489 volt lower (more electropositive) than the initial contact difference of potential when no hydrogen was present. To check these results, the experiment was now reversed. The hydrogen was gradually pumped off and replaced by air. This decrease in concentration of the hydrogen resulted in a similar series of curves ending in the initial results of the previous experiment. This final value was not attained, however, until the carbon had been baked in an electric vacuum furnace.

The other metals were cleaned with glass paper, another series scraped with a steel tool, and then examined under similar conditions explained above. They exhibited changes similar to those shown by the carbon but neither were they so pronounced nor was the occlusion of hydrogen so simply controlled.

The experiment was also repeated with cocoanut charcoal, whose gas had been removed through heating (above 550° C.) in an electric vacuum furnace. These results contributed nothing to those quoted above.

Results from Carbon Saturated with Other Gases.—Similar pieces of charcoal from the same stock were now examined for changes in contact difference of potential in the presence of and saturated with dry ozone, oxygen, air, carbon dioxide, nitrogen and ammonia. The curves resulting through the presence of these gases in the carbon are shown in Fig. 4.

The carbon was not only saturated with the gas, but the measurements were also made with that particular gas filling the chamber. Any other combination, such as replacing the gas in the chamber by means of dry

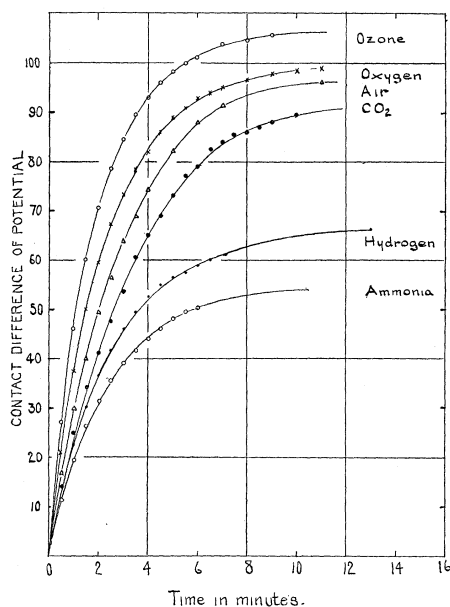


Fig. 4.

air, resulted in diffusion of the occluded gas from the carbon, accompanied by a corresponding upward shift of the values, as shown with hydrogen. The curve for nitrogen was omitted due to its proximity to that of carbon dioxide.

The ozone used in these experiments was collected from the immediate vicinity of a 110-volt quartz mercury vapor lamp. The lamp was enclosed in a small box and the gas drawn out of this compartment, after the lamp had been burning several hours. This and the other gases were all dried through the phosphorous pentoxide tube described. The oxygen was the commercial type derived from liquid air. The nitrogen was generated by heating ammonium nitrite. It was purified by passing it through sodium hydroxide and thence over glowing copper gauze. The ammonia was acquired by heating chemically pure concentrated ammonium hydroxide and then dried in the usual way.

The order in which the equilibrium values of the carbon, saturated with these gases appear, is of interest in so far as they are identical with the Volta series for these gases as determined by Grove,¹ in his experiments

¹ Grove (Phil. Trans., 1845), Winkelmann's Handbuch, Vol. 2, Elect. and Mag., p. 181.

on gas cells. Similar series by Becke¹ and Gore² are quoted for comparison. The last column in the table shows the observed equilibrium value of the contact electromotive force in volts, attained by the carbon, satu-

Volta Series for Gases.

Grove.	Becke.	Gore.	S	Equilibrium Values in Volts.
+				
Metals that decompose water				
NH ₃			NH ₃	.079
H ₂	H ₂	H ₂	H ₂	.096
CO				
Alcohol				
Aether				
Camphor				
Metals insoluble in water				
N ₂		N ₂	N ₂	.129
CO ₂	Air		CO ₂	.130
NO	CO ₂		Air	.136
O ₂			O ₂	.142
O ₃			O ₃	.155
I		I		
Br		Br		
Cl		Cl		
—		O ₂		
		Fl		

rated with these gases, when the opposing plate of copper oxide was at a zero potential.

It might be of interest to compare the value obtained for "air" with that computed from the values of nitrogen oxygen and carbon dioxide, taken in the proportion in which they occur in air.³ The latter gives .132 volt as against the observed value of .136 volt.

Conclusions in Regard to the Effect of Dry Gases.—In view of the above data it seems essential to know or be able to control the previous history of a metal before values of contact electromotive force can be accepted with any reliability. The intrinsic potential can be determined only after all occluded and surface gases are removed. That the removal of all gases is difficult and often impossible, was shown by the recent experiments of Hughes.⁴ He has shown what a tremendous influence the entrance of the slightest trace of air may have on the contact potential

¹ A. Becke, Ann d. Phys., 29, 5, pp. 909-940 (1909).

² G. Gore, Cooper's "Primary Batteries," p. 19 (1901).

³ Phys. Chem. Const., Kaye and Laby, p. 125. Composition of air by volume, N₂ 78.05, O₂ 20.91, CO₂ .03 to .3, A .95.

⁴ Ll. Hughes, Phil. Mag. (6), 28, p. 337 (1914).

of metals distilled in a very high vacuum. Another point of interest, in this connection, is the supposed absence of gases on the surfaces of metals like Na, K and Li freshly cut in vacuo.¹ The surfaces are not here necessarily exposed to the residual gases in the vessel, they are however exposed to the occluded gases which constantly leak to the surface from the depths of the metal itself.

In a very exhaustive paper Murray² showed that if a plate of zinc is polished with glass paper, it attains a potential .70 volt positive to a standard gold plate. If it is now burnished with a tool of hardened steel it will rise to a nearly permanent value of .94 volt. This "seeming inexplicable³ electropositive increase" of .24 volt through burnishing can however be explained in terms of our occlusion experiments. They show that, as the concentration of the hydrogen occluded near the surface increases, the equilibrium values become more electropositive. Now zinc in common with all other metals can occlude gas to a certain extent. The surface layer of the zinc, under the influence of the pressure exerted by the burnishing tool becomes more compact. This packing is accompanied by a corresponding concentration of the occluded gas in this layer. Hence such and other mechanical concentrations must necessarily result in a more electropositive value for the contact potential.

In a similar way all mechanical processes that produce fresh surfaces on a metal, through the removal of the old one, must result in a gradual accumulation of gas on this new surface, which again results in a positive shift of the C.D.P. And a shift to more positive values in the C.D.P. gives us a corresponding shift of the red wave-length limit towards positive values as Millikan⁴ has recently shown, in his experiments on the photoelectric effect. A similar photoelectric shift should result if a metal originally having occluded a very electronegative gas, had that gas replaced by means of a very electropositive one.

The above parallelism between photoelectric shift in the red wave-length limit and contact difference of potential is very interesting, since it leads us to think that the occlusion of gases, up to a certain degree, offers the electrons in the metal a means of decreasing their affinity for the atoms.

Experiments on the Influences of Water-vapor.—If water-vapor had been present in the gases during the previous experiments, the variations of the contact electromotive force would have been more complex. The

¹ K. T. Compton, *Phil. Mag. Ap.*, p. 579 (1912). R. A. Millikan, *PHYS. REV.*, 7, p. 366, also p. 374 (1916).

² E. Murray, *Proc. Roy. Soc.*, 63, p. 113 (1898).

³ Lodge, *Phil. Mag.*, XLIX., p. 371 (1900).

⁴ R. A. Millikan, *loc. cit.*

results obtained under these conditions have, however, some things in common. Independent of the kind of metal or gas used, what at first sight passed for contact electromotive force, rises to a maximum and then gradually drops off to an equilibrium value, as time goes on.

Similar variations have been observed by investigators referred to above. More recently Lose¹ has found similar variations in his experiments on the influence of glow-discharge on the volta-effect.

After eliminating all extraneous causes of contact electromotive force and using very pure gases in the presence of water vapor, one finds that the complex variations can in general be represented by such a double exponential curve as shown in Fig. 2. The curve with increasing values of time was found to rise exponentially to a maximum, then fall off exponentially to an equilibrium value. The initial rise is similar to that discussed under the effect of dry gases, superimposed on this effect is the exponential decrease due to the presence of the vapor.

In the presence of any of the above gases and water-vapor similar variations are observable, but the magnitude and appearance of the maxima, and the absolute value of the end or equilibrium values are different.

Cocoanut charcoal was again resorted to in studying this effect. The strip of gas-free carbon was placed in the chamber and the gas under examination mixed with water vapor was allowed to enter the vessel. Later this was varied by examining the carbon in the presence of the dry gas, then reexamining it when a few drops of water were introduced into the bottom of the cylinder. This was enough to produce the desired saturation at room temperature. For the sake of clearness only a few of the representative values are given. The first curve to the left in Fig. 5 showing a pronounced maximum was obtained in the presence of air and saturated water vapor. The curve rises to a maximum of $-.141$ volt after 52 seconds from the time at which the carbon's potential became active through opening of the earthed key connecting the plate to the electrometer, from this point the potential gradually fell to -0.014 volt after an elapse of six minutes. The curve below it shows the results obtained when the air is replaced by hydrogen also saturated with water-vapor. The maximum is not so pronounced and only attained -0.0391 volt after 200 seconds. Similar experiments with platinum and palladium produced similar effects though the maxima and end values were different.

Experiments with Other Vapors.—The second series shown to the right in Fig. 4 represents identical experimental conditions as the previous ones,

¹ A. S. Lose, *Deutsch. Phys. Ges. Verh.*, 17, 1, p. 3 (1915).

with this exception, alcohol-vapor was substituted for water-vapor. All the maxima were higher and the time of their appearance was very much greater. The end values, even after several hours, were not as low as those reached by the metal in the same gas saturated with water-vapor. Experiments with the vapors from turpentine and soft wax produced still larger changes in the time of appearance of the maxima. In addition the rate of increase and decrease of the potential near the maxima is very slow and often imperceptible; so much so that the results may be mis-

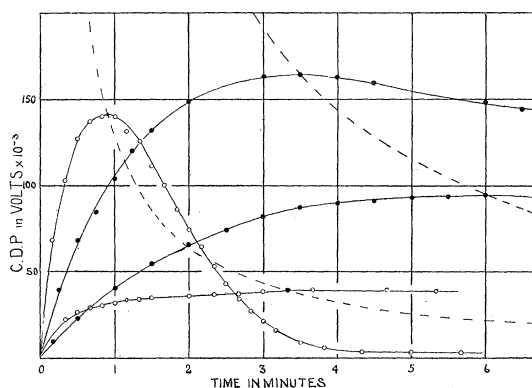


Fig. 5.

taken for the pure exponential curves common to the results discussed under variations in the presence of dry gases.

The above series and similar ones for other metals, lead to some very interesting conclusions in regard to what have heretofore passed as contact electromotive forces. The subsequent lowering of the contact potential has usually been attributed to the presence of hydrogen peroxide. The hydrogen peroxide was assumed to attack the metal and form a secondary reaction, resulting in the change leading to an equilibrium value. This secondary reaction is however improbable in ammonia or nitrogen saturated with water-vapor or alcohol-vapor, in which nevertheless the rise to a maximum and subsequent drop to an equilibrium value occurs. Of course one might argue for the presence of this secondary reaction through the well-known catalytic power of carbon or platinum. But would such a reaction result in the formation of a free charge, contributing its share to the charge accumulated by the electrometer?

A more promising explanation is offered when we consider the possibilities introduced by the polarization of the metal surface under investigation.

Polarization Theory.—In a primary cell, the reduction in the electro-

motive force due to an alteration of the electrolyte or of the plates, brought about by the voltaic action of the cell is known as polarization.¹ Our experimental conditions are such that they may be considered acting like a primary cell, the necessary current being supplied by the constant source of ionization. This ionization current may be considered as moving towards the carbon plate under the action of the potential gradient due to the intrinsic contact difference of potential between it and the copper oxide cylinder. The cylinder is constantly kept at a zero potential, while the carbon plate, initially at zero, is connected to the electrometer when the circuit is under examination. The electrometer therefore measures the variations taking place at the carbon plate and at such points in its immediate neighborhood as can influence its potential.

Let us first consider the conditions involving no polarization, namely, those results obtained from the variation of the contact difference of potential in dry gases. The exponential curve attains a maximum potential V' after an infinite time. Let V be the instantaneous value of the potential as indicated by the electrometer. Let the system have a capacity C such that $Q = Ne = CV$. Then

$$\frac{dN}{dt} = \frac{C}{e} \frac{dV}{dt}.$$

Let

$$\frac{dN}{dt} \propto (V' - V);$$

then

$$\frac{dN}{dt} = k(V' - V) \quad (1),$$

where the constant k denotes the rate of appearance of the ions at the plate, it also depends on c/e , on the kind, concentration and density of the gas, on the velocity of the ions, etc. Solving² this equation for the instantaneous value that the potential may attain, we get

$$V = V'(1 - e^{-kt}), \quad (2),$$

an expression which when plotted corresponds to our various curves for dry gases. For example the hydrogen change in concentration curves may now be represented by simply varying the values of k in the above equation. Increasing values of this constant takes us step by step from the lowest curve, representing maximum concentration, to the highest one, representing zero concentration. Hence k is inversely proportional to the property of the occluded gas, contributing to the variation from the intrinsic contact potential.

¹ Cooper, Primary Batteries, 1901.

² I am indebted to Professor Horace C. Richards for valuable suggestions involved in this analysis.

If a vapor is now introduced, our experimental values lead to a secondary reaction resulting in polarization. Under these conditions the above V' becomes a variable, through the variation contributed by the polarization. Again let

$$\frac{dV'}{dt} = -k'V',$$

where the negative value of the constant k' denotes the rate of decrease through polarization action. It also depends on the current density, temperature, character of the electrode, etc. Solving for V' we get

$$V' = V_0 e^{-k't}, \quad (3)$$

which in combination with equation (1) gives

$$\frac{dV}{dt} + kV = kV_0 e^{-k't}, \quad (4)$$

whose solution is

$$V = V_0 \frac{k}{k+k'} (e^{-k't} - e^{-kt}) \quad (5)$$

where the constant V_0 is the contact difference of potential when the polarizing influence is removed. This is the double exponential curve which fits all the results when polarization takes place through the presence of a vapor.

The equation has a maximum for values of t given by

$$\frac{k'}{k} = e^{(k-k')t}.$$

This result possesses a special interest in so far as it states that the maxima of all curves developed from any particular metal in the presence of any gas, saturated with a particular vapor, must lie on the logarithmic curve characteristic of this group of limitations. For example if $k'/k = 68.5$ and plotting k' against time we get the dotted logarithmic curve passing through all the maxima of the left group. For the above ratio equal to 6,380 we get a corresponding curve through the maxima of the group on the right.

Intermediate values of this ratio produce corresponding curves passing through the maxima of the curves from the various mixtures of concentrations of alcohol and water.

Conclusions.—Variations in contact difference of potential of a specific metal are primarily due to the kind and concentration of the occluded gas in the metal.

Successive increases in concentration of the occluded gas produce successive decreases in the electronegative magnitude of the contact difference of potential, a property common to all gases.

All mechanical processes affecting the surface layers of the metal tending to increase the concentration of the occluded gas produce the same change.

The gases ozone, oxygen, air, carbon dioxide, nitrogen, hydrogen and ammonia if occluded by a metal, shift the position of the metal in the Volta series to a more electropositive value in the order in which they are named. Changes in contact difference of potential were found for gases and vapors which cannot form hydrogen peroxide to explain the secondary reaction. These and similar changes in contact difference of potential involving secondary reactions, can be explained with a polarization hypothesis.

The degree of polarization depends on the relative electronegative properties of the gases and vapors in which the contact difference of potential is measured.

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