These results indicate that the composition of the acid carbonate of barium in dilute solution at 15 to 16° C. has a composition expressed by the formula $BaCO_3.1.5(H_2CO_3)$. This confirms the results that we obtained from the analysis of the precipitated acid barium carbonate.

The experiments described in this paper were made in January and February, 1908, and it is our intention in the coming winter to apply the methods described to the determination of the composition of the acid carbonates of other metals.

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THE PASSIVE STATE OF METALS.

A REVIEW OF THE LITERATURE AND THEORIES AND SOME EXPERIMENTS ON COBALT, IRON AND NICKEL.

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Received July 14, 1908.

Contents.—(1) Introduction; (2) Periods of Investigation and References; (3) Theoretical; (4) Experimental—(*a*) Cobalt, (*b*) Iron, (*c*) Nickel; (5) Summary.

Introduction.

The literature upon the subject of passivity is already enormous and is rapidly accumulating in recent years. The theories and views are also rather numerous and conflicting. It seemed to me, therefore, it would be of assistance to chemists and perhaps stimulate work in this field if, in connection with my experimental work on cobalt, iron and nickel, I should give an outline of the literature and a brief review of the theoretical views. Several reviews have been published at various times, each with more or less complete references to the literature. These are as follows: Schönbein, "Das Verhalten des Eisens zum Sauerstoff," Basel (1837); Berzelius, *Lehrbuch*, Vol. II, p. 692 (1844); Wiedemann, *Lehrbuch der Electricität*, Vol. II, p. 812 (1894); Ostwald, "Electrochemie, Ihre Geschichte und Lehre," p. 696 (1896); Sakur, *Chem.-Ztg.*, **28**, 954 (1904); Fredenhagen, *Z. physik. Chem.*, **63**, 1 (1908). All of these are in German, and while it might seem desirable to publish such a review in English,[1] the recent work of Fredenhagen would have deterred me were it not for the fact that he leaves out of sight the early literature and approaches the later work as an advocate for his own theory.

For the purpose of presentation it is perhaps convenient that the material presents itself in three rather well defined periods: (1) From the discovery of the phenomenon to the close of Schönbein's work, 1790–1838. (2) From Schönbein to Hittorf, 1838–1898. (3) The recent development, 1898——.

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[1] Heathcote, *J. Soc. Chem. Ind.*, **26**, 899 (1907), gives a list of references of the early literature but the journal is not to be had in Leipzig, and I am unaware as to how complete it is.

Literature, First Period.—Passivity of metals was first observed in iron and the discovery is usually ascribed to James Keir[1] in 1790, although it had been previously noted by Bergman[2] that iron does not cause the precipitation of silver from silver nitrate. Keir's investigation was fairly thorough in that he noted the initial precipitation of silver and its subsequent solution with the formation of a bright iron surface. He noted the failure of iron to dissolve in concentrated nitric acid and its renewed activity when touched with fresh iron. He also called attention to the superficial character of the change and to the difficulty of so cleaning and drying the iron as to cause it to retain its inactive properties.

The work of Keir seems to have been quite forgotten and the phenomenon was rediscovered by Wetzlar[3] and recognized by him as electrochemical in its nature. The first paper of Wetzlar was followed by Fechner[4] who not only developed the subject by determining the direction of the electric current in a cell using iron and silver as electrodes but republished the work of Keir.[5] Both these investigators as well as Sir John Herschell[6] pursued their investigations and showed that the position of passive iron in the electrochemical series is below that of silver; that the passive state is produced in ordinary nitric acid by contact with metals below it in the electrochemical series and destroyed by those above it. The periodic passivity and certain other conditions were brought to light.

The behavior of iron was also thoroughly investigated by Schönbein,[7] to whom we owe the terms 'passive' and 'active' as denoting the different states of iron with respect to its behavior in nitric acid and as an anode. An interesting phase of Schönbein's work was the communication of his first results by letter to Faraday with a request for an explanation. Faraday[8] published the letter together with the requested explanation and some observations of his own. The explanation will be fully considered later. It is, in substance, that a coating of oxide is formed over the metal. In subsequent work Schönbein vigorously assailed the view of passivity set forth by Faraday as well as one proposed by Mousson.[9] He also confirmed certain observations by Andrews[10] relative to the passivity of

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[1] James Keir, *Phil. Trans.*, 80, 359 (1790).

[2] Bergman, Dissertat. divers. phlogist. quantit. Metals.

[3] Wetzlar, *Schweigger's Jour.*, 49, 470 (1826); 50, 80, 129; 56, 206.

[4] Fechner, *Ibid.*, 53, 141 (1828); 61, 129; *Pogg. Ann.*, 47, 1 (1839).

[5] Keir (Fechner), *Ibid.*, 53, 151.

[6] Herschell, *Ann. chim. phys.*, 54, 87 (1833); *Pogg. Ann.*, 32, 211 (1834).

[7] Schönbein, *Phil. Mag.*, 9, 53 (1836); *Pogg. Ann.*, 37, 390, 590; 38, 444, 492 (1836); 39, 137, 342, 351; 43, 1 (1838); 13, 103; 40, 193, 621; 41, 41, 55; 59, 149.

[8] Faraday, *Phil. Mag.*, 9, 53; 10, 175; also *Exp. Researches*, Vol. II, p. 231.

[9] Mousson, *Pogg. Ann.*, 39, 330.

[10] Andrews, *Phil. Mag.* [3], 12, 305 (1838); *Pogg. Ann.*, 45, 121; *Proc. Roy. Soc.*, 48, 116; 49, 481.

bismuth and tin. His most important contributions to the subject were the demonstration of the passivity of iron as an anode in salt solutions of oxygen compounds, the activity of iron under all conditions in solutions of the halogen acids, and the active or passive state in oxygen acids according to the method used for closing the circuit.

Minor papers were contributed also by Fischer[1] and Schweigger and Siedel.[2] The work of Schönbein may be said to close the first period, the net results of which may be summed up as follows: The fundamental facts in regard to the passive state of iron, the means of producing and destroying it, and the Faraday explanation of its cause were developed. Also three other metals were shown to assume under certain circumstances a similar inactive state, *viz.*, tin, copper, bismuth. A further important result was in connection with the then unsettled question as to the source of voltaic electricity, since, as Schönbein and Faraday had shown, a cell made up of passive iron, platinum and nitric acid gave no current; but if the iron were touched beneath the liquid by copper or zinc a current was immediately produced and continued to flow. This fact was a strong argument in the hands of Faraday against the "contact theory" of Volta.

Second Period.—The literature of what I have called the second period is very voluminous, yet but little advance was made beyond the point reached by Schönbein.

The most important work was that of Beetz[3] who in a series of articles reviewed all previous work and tested the results. His general conclusion was that the hypothesis of Faraday was correct and while he himself did not decide in favor of any definite oxide, Wiedemann, in his *Lehrbuch* previously referred to, used his results and assumed the oxide to be Fe_3O_4, and this statement finds wide expression through text-books.

Nickles[4] added nickel and cobalt to the list of anodic inactive metals. Nichols and Franklin[5] showed that, as Andrews had also shown, magnetization not only did not produce but destroyed the passive condition, and that iron continued to dissolve slowly in nitric acid when passive, a fact which, if it be a fact, is utterly at variance with Faraday's theory. Corsepius[6] also by measurements of the electromotive force of passive iron with reference to an unpolarizable zinc electrode showed that there were various degrees of passivity; at least a variable e. m. f. could be produced.

[1] Fischer, *Pogg. Ann.* [2], **6**, 43.

[2] Schweigger and Siedel, *Schweigger's Jour.*, **53**, 170 (1828).

[3] Beetz, *Pogg. Ann.*, **62**, 234; **63**, 415 (1844); **67**, 186 (1846). *Rep. Physik.*, **8**, 256 (1849). *Pogg. Ann.*, **127**, 45 (1866). *Wied. Ann. N. F.*, **2**, 94 (1877). *Münch. Ber.*, **1875**, 59. *Wied. Ann.*, **156**, 464.

[4] Nickles, *Compt. rend.*, **37**, 284 (1853). *Pogg. Ann.*, **90**, 351.

[5] Nichols and Franklin, *Am. J. Sci.* [3], **31**, 272 (1886); [3] **34**, 419 (1887).

[6] Corsepius, Dissertation, München, 1887; *Beiblätter*, **11**, 242.

Wöhler[1] showed that very frequently meteoric-iron is passive. Buff,[2] starting from an observation of Wheatstone, showed aluminium to be passive under a large variety of conditions and the development of this subject and the assumption that the passivity of aluminum is due to an oxide coating, which under some circumstances, certainly, is formed, no doubt helped to fix the oxide theory in the minds of chemists and physicists.

What I think is practically a complete list of these "middle age" contributions follows:[3]

Third Period.—The modern development of the subject dates from the classic researches of Hittorf[4] on the passivity of chromium and iron.

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[1] Wöhler, *Pogg. Ann.*, **85**, 448.

[2] Buff, *Liebig's Ann.*, **102**, 265 (1857).

[3] Martens, *Pogg. Ann.*, **55**, 37 (1842); **63**, 412 (1845); *Mem. d. Bruxelles*, **19**, 21. Grove, *Phil. Mag.* [3], **15**, 292 (1839); *Pogg. Ann.*, **49**, 600 (1840); **63**, 424; *Arch. d. l'Elec.*, **4**, 167. Wheatstone, *Phil. Mag.* [4], 10, 143 (1854). Wöhler and Buff, *Ann.*, **103**, 218 (1858). Joule, *Phil. Mag.* [3], **24**, 108 (1844). Ohm, *Pogg. Ann.*, **63**, 389 (1854). Oudray, *Am. J. Sci.* [2], **40**, 316 (1865). Schönn, *Z. anal. Chem.*, **10**, 291 (1871); *Arch. Phys.* [2], **43**, 186. Rénard, *Compt. rend.*, **79**, 159 (1874); **79**, 508. Regnon, *Ibid.*, **79**, 299 (1874). Varrenne, *Ibid.*, **89**, 780 (1879). Held, *J. prakt. Chem.*, **90**, 268 (1883). St. Edine, *Compt. rend.*, **52**, 920; **106**, 1079 (1888); **109**, 304 (1889). Ducretet, *J. Physik.*, **4**, 184 (1875); *Compt. rend.*, 80, 280 (1875). Oberneck, *Wied. Ann.*, **19**, 625 (1883). Pollak, *Compt. rend.*, **124**, 1443 (1897). Grätz, *Wied. Ann.*, **62**, 323 (1897). Strenitz, *Ibid.*, **34**, 751 (1888); **32**, 116. Laurie, *Phil. Mag.* [5], **22**, 213, 1886. Scott, *Wied. Ann.*, **67**, 388 (1899). Lecher, *Ber. Wien. Akad.*, **107**, 2a, 739 (1898). Guthrie, *Phys. Review*, **15**, I, 327. Norden, *Z. Electrochem.*, **6**, 159 (1899). F. Fischer, *Ibid.*, 10, 869; *Z. physik. Chem.*, 48, 177 (1904). R. Way, *Z. öffentl. Chem.*, **9**, 158. Ditte, *Compt. rend.*, **110**, 573; **128**, 195; *Ann. chim. phys.*, **7**, 16. Askenay, *Z. Elektrochem.*, 4 (67), 70 (1897). Taylor and Inglis, *Phil. Mag.* [5], **27**, 301 (1903). Schulze, *Ann. Phys.* [4], **21**, 929 (1906); [4], **22**, 543; **23**, 326. *Ibid.* [4], **24**, 43; **25**, 773; *Z. Elektrochem.*, **14**, 333 (1908). I have included in the above list all references to the passive condition of aluminium whether later than 1898 or not.

[4] Hittorf, *Z. physik. Chem.*, **25**, 729 (1898); **30**, 480 (1899); **34**, 385 (1900). Micheli, *Arch. sci. phys. nat.* [4], **10**, 122 (1900). Heathcoate, *Z. physik. Chem.*, **37**, 368 (1901); *J. Soc. Chem. Ind.*, **26**, 899 (1907). Finkelstein, *Ibid.*, **39**, 91 (1902). Ostwald, *Ibid.*, **35**, 33, 204 (1900). Brauer, *Ibid.*, 38, 441 (1901). Mugdan, *Z. Electrochem.*, **9**, 442 (1903). LeBlanc, *Ibid.*, 6, 472 (1900); **11**, 9 (1905); also Lehrbuch. LeBlanc and Levi, Boltzmann's Festschrift, p. 183 (1903). Rener, *Z. physik. Chem.*, **44**, 81 (1903); *Z. Electrochem.*, **11**, 661 (1905). Brochet and Petit, *Bull. soc. chim.* [3], **31**, 742. Fredenhagen, *Z. physik. Chem.*, **43**, 1 (1903); 63, 1 (1908); *Z. Electrochem.*, **11**, 857 (1905). Sakur, *Ibid.*, **10**, 841 (1904). Muthman, *Ibid.*, **10**, 521 (1904). Muthman and Frauenberger, *Ber. Bay. Akad.*, **34**, 201 (1904). Marino, *Gaz. chim. ital.*, **35**, II, 193 (1905). Müller, W. J., *Z. physik. Chem.*, **49**, 577; *Z. Electrochem.*, **10**, 518; **11**, 755, 823. Königsberger and Müller, *Phys. Zeit.*, **5**, 415, 797 (1904); **6**, 847; **7**, 796; *Z. Electrochem.*, **13**, 659 (1907). F. Fischer, *Z. physik. Chem.*, 48, 97 (1904). Cohen and Osaka, *Z. anorg. Chem.*, **34**, 86 (1903). Haber and Goldschmidt, *Z. Electrochem.*, **12**, 49. Hollis, *Carub. Phil. Soc.*, **12**, 462. E. Müller and Spitzer, *Z. anorg. Chem.*, **50**, 321 (1906). A. Kreussler, *Chem.-Ztg.*, May 13, 1908, 476. Forster and Pignet, *Z. Electrochem.*, **10**, 714 (1904). LeBlanc and Byers, *Z. Electrochem.*, 1908.

That his work has caused a revival of interest in the subject is due in part to the threefold manner of solution of chromium as an anode, while still capable of solution showing all the features of the practically insoluble passive iron; in part to his vigorous exposition of the insufficiency of Faraday's theory, and also to the extension of the list of passive metals.

This period is also almost as fruitful in theories as in experimental contributions and most of the researches are accompanied by more or less extended theoretical discussions. In some cases indeed we have theoretical discussion with no research.

It is as yet impossible to say what the result of this period of activity is, since there has been no masterly research or exposition since Hittorf's and the last word, and very likely the last theory, are very far in the future. I introduce the preceding list of references to avoid repetition in the theoretical and experimental portions of the paper.

Theoretical.

The term 'passive' was first employed by Schönbein to describe the peculiar condition assumed by iron under certain circumstances. It was recognized very early that an intimate connection existed between this passive state and its electrochemical relations. This connection has been greatly emphasized by subsequent research. The term as now used is not very exact, but in general it applies to the condition of an element when it shows abnormal electrochemical relations and a chemical inactivity not corresponding to its ordinary behavior and not in accord with its position in the electrochemical series.

Usually also we do not use the terms when we can easily determine the existence of a medium of separation of the element from the other active factors present or when the electrochemical condition remains constant.

In general we find that, with reference to their behavior as anode, the elements divide themselves into three distinctly marked groups.

(1) Elements which as anodes go into solution quantitatively under the influence of the electric current and conform to Faraday's law.

(2) Elements which as anodes ordinarily fail to go into solution with the electric current.

(3) Elements which under different conditions belong to both of these classes; or, if soluble in all conditions as anodes, the character of the process is not always the same.

In connection with passivity then we are concerned only with the last group. However, in certain cases this anodic relation manifests itself only when the metal is used as an anode, and the cause can clearly be referred to a *visible* coating of oxide or similar insoluble material and no other anomalous behavior of the element is observed. There is a strong tendency in the literature to exclude such cases from the class of passive elements.

In many cases we find that not only does the element under specific conditions alter its anodic behavior, but that this condition may be variously produced and manifests itself by altered properties in the absence of electrical currents. Moreover, it is usually impossible to *see* any material cause for the change in properties. These last cases we may call truly passive elements.

In the history of the subject we find a variety of views of the nature of passivity and a number of explanations as to its cause. Naturally up to 1898, the matter concerns itself chiefly with iron.

The following list gives in brief the suggestions which have been offered.

(1) Fechner: Considered and rejected the hypothesis of an insoluble protective coating (1828).

(2) Herschell: The passive state is due to a certain 'permanent electrical state' of the metal (1833).

(3) Faraday: The metal is protected by a layer of oxide (1836).

(4) Mousson: The passive state of iron in nitric acid is due to a protective layer of nitrous acid (1837).

(5) Schönbein: The solutions in which iron is passive exert a negative catalytic effect on the chemical activity of the iron (1837).

(6) Hittorf: Passivity is due to an induced change in the nature of the metallic surface (Zwangzustand) (1900).

(7) Finkelstein: The metal is transformed into a nobler modification represented by changes in valency (1902).

(8) W. J. Müller: The passive state is due to a change in valency produced by varying electron density (1904).

(9) LeBlanc: The passive state is due to a change in the velocity of ionization of the metal (1903) (1906).

(10) Fredenhagen: Passive state is due to change in velocity of reaction between metal and anodic oxygen (1903) (1908).

There need be but little said about suggestions 1, 2 and 4 given above. The first is merely negative, the second indefinite and unfruitful, and the fourth manifestly incorrect, since the phenomenon is not confined to nitric acid.

The explanation offered by Faraday was made, in response to the previously mentioned request of Schönbein, in the following terms: "My strong impression is that the surface of the iron is oxidized, or that the surface particles are in such relation to the oxygen of the electrolyte as to be equivalent to oxidation; and having thus their affinity for oxygen satisfied and not being dissolved by the acid under the circumstances, there is no renewal of the metallic surface and no reiteration of the attraction of the successive particles of iron on the elements of successive particles of the electrolyte."

This view was strongly opposed by Schönbein on many grounds but chiefly, perhaps, because iron could be maintained in the passive state in dilute nitric acid, which ought to dissolve any oxide if it were formed. Faraday acknowledged the weakness of his suggestion but protested that it was the best he had to offer and adds that he did not assume the protective layer to be due to a known oxide of iron, none of which satisfy the conditions, but that the state is rather one of a "very delicate equilibrium." In spite of this equivocal support of Faraday, the pronounced opposition of Schönbein and its draft on the imagination, the influence of the name of Faraday, the work of Beetz and the text of Wiedeman, with its gratuitous assumption of the oxide Fe_3O_4, combined to give this view general credence until the time of Hittorf. The contributors to the literature during the past ten years, with the exception of Haber and Goldschmidt, E. Müller and Spitzer, and Heathcote, unite in rejection of the Faraday view, if they fail to agree in any other particular.

The more important grounds upon which this rejection is based are given in the enumerated list below.

(1) The passivity of both iron and chromium must be assigned to unknown oxides. The known oxides do not produce it. These oxides must be very unstable because of the ease of transformation of the one condition to the other (Hittorf).

(2) The influence of increase of temperature is to destroy and not to cause passivity (Hittorf).

(3) The oxide must be a good conductor of electricity (Ostwald).

(4) The assumption does not explain the increase of negative potential of the passive metals (Finkelstein).

(5) The passivity of chromium does not cause a cessation of solution but a change in its character (Hittorf).

(6) The curves of the potential required to make the metals passive do not show a definite point corresponding to the formation of a definite oxide (Fredenhagen, see remarks on his theory).

(7) If to electrolytes which form an insoluble deposit on the anode be added a large excess of an electrolyte which forms soluble compounds with the anode the insoluble material may be collected as a precipitate falling from the anode, which continues to dissolve (The Luckow phenomenon, Le Blanc and Binschedler[1]).

This reaction occurs in the case of nickel as an anode in alkaline solutions with a large excess of common salt, but under similar conditions also with nitrates, sulphates and chlorates, in all of which nickel is passive, and no trace of insoluble material can be observed (LeBlanc and Levi, *loc. cit.*).

(8) Passive metals can be made to assume a high potential in electrolytes and lose this partially or completely when placed in air or in a vacuum or on being washed and dried. This would correspond in terms of the

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[1] *Z. Elektrochem.*, 8, 25.

Faraday hypothesis to a reduction of the oxide by *air* (Muthman and Franenberger, Heathcoate, etc.).

(9) All efforts to demonstrate the presence of a layer of oxide by optical means result negatively (Königsberger and Müller (W. J.)).

(The references to the literature cited previously are not repeated.)

The foregoing, together with many other objections which might be urged, are so convincing that we may well assent that the Faraday hypothesis may be laid to rest.

The view of Schönbein is not an explanation and has but little value except as expressing his recognition of the mutual nature of the condition with reference to electrolyte, or solvent, and metal. He himself says that such hypotheses are only "Eselsbrücken."

Hittorf, sixty years later, makes the next variation. To be sure, he ventures no suggestion as to the nature of the forces which give rise to the 'Zwangzustand' which he assumes as the immediate reason for the high negative potential and varied solubility of the passive metals. Neither does he express himself as to the character of the change in the metal itself except to suggest that it recalls the alchemistic transmutation of metals. His view-point is interesting chiefly as it leads directly to the explanations developed by Finkelstein and by Müller. Finkelstein's explanation seems not to have been very well digested, as he himself apparently recognizes. It must be confessed, however, that the fundamental idea, that of a changed valency as the immediate forerunner of the other phenomena of passivity, is very attractive. Moreover, the suggestion fits in well with the behavior of chromium and of molybdenum, which certainly go into solution in different states of oxidation in the active and passive states. Whether this is a primary or secondary result is, however, not clear.

On the other hand, the evidence he brings in favor of a state of equilibrium between ferro and ferri ions in passive iron is not at all convincing.

The same fundamental idea is reached by W. J. Müller, who bases his conception on the electron theory and states it as follows: "Das Gleichgewicht zwischen Electronen and Metallionen verschiebt sich bei verschiedener Electrondichte sprungweise, daraus folgt, dass dem passiven Verhalten Wertigkeitphänomene zu Grunde liegen."[1]

He considers the various stages of valency as solid phases, and that one phase is transformed into the other at a definite electron density and finally that the various means of making metals passive are means of effecting the required density. The chief differences from Finkelstein's view are in the point of departure, and the assumption of a sudden 'sprungweise' transformation as opposed to a state of equilibrium in which both, or several, degrees of valency are present. In the case of iron, also, he

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[1] *Z. Elektrochem.*, 10, 832.

assumes the passive state to be not the trivalent but the sexivalent condition.

It is perhaps difficult to reconcile this view with the gradual anodic potential change of passive metals which has been shown (Hittorf, Muthman and Fredenhagen) to exist and which potentials Müller assumes as the surest criterion of passivity and which define the various stages of valency (see particularly the recent experiments of Fredenhagen).

Müller also recognizes that his view does not show in any way how the different electrolytes affect the electron density.

The view of LeBlanc, like those of Schönbein and Hittorf, is not an explanation of the course or causes of the phenomena of passivity but has its value in that it recognizes the important rôle played by both electrolyte *and* metal and in that it points out the class of reactions to which the origin of passivity is perhaps due. The conception that the rate of ionization of a metal is not always infinitely great is not revolutionary, and the idea that current density or various reagents modify it, is a perfectly natural consequence. *How* this change is brought about or *why*, LeBlanc has not yet ventured to say. He has work on the subject in progress and we may expect a development of his views in the near future. If he can demonstrate that in the passive condition the rate of ionization or the solution pressure of the metals is altered, he will have made a material advance.

Fredenhagen (supported by Muthman and Franenberger) starting from this conception of velocity of reaction has developed a view which is after all but a modification of that of Faraday. It is to the effect that anodic oxygen depresses the velocity of reaction between the metal and itself to such a point that the anode covers itself completely with a layer of oxygen or forms an alloy of metal and oxygen which prevents further action, *i. e.*, produces the passive state. According to Fredenhagen this conception is free from the objections to the oxide hypothesis. Indeed it differs very slightly from Faraday's state of 'very delicate equilibrium.'

It must be admitted that this explanation is in accord with most of the phenomena of passivity, and granting the initial separation of anodic oxygen it accounts for the varying anodic potentials measured by Hittorf, Muthman and Franenberger, Fredenhagen and others. That is, these negative potentials are due to an oxygen electrode and increase or decrease in potential with the concentration of the oxygen. It is however difficult to account by anodic oxygen pressure for the passive condition of iron in potassium cyanide and other reducing agents in which it can be made passive, or for the passive condition of chromium in hydrochloric acid.

If, however, chlorine does not prevent the separation of anodic oxygen the question arises as to why, in the case of passive nickel in sulphates, nitrates, etc., the passivity is destroyed by addition of halogen salts. The oxygen layer would also seem to fail to account for the loss of the passive state in the magnetic field, in the case of iron.

It also fails to accord with certain of my own observations, mention of which is made in the experimental portion.

Having thus briefly reviewed the theoretical situation I will, after reporting my experiments, summarize my conclusions from experiment and literature.

Experimental.

The work on passivity of metals up to the present time has been confined largely to qualitative tests of the behavior of the metals when passive, to the means of producing and destroying the passive condition, and to measurements of potential of the anode. The most notable exceptions to this statement are found in the work of Hittorf, LeBlanc and Levi and Marino.

At the suggestion of Prof. LeBlanc, I undertook a series of measurements of the anodic solution of cobalt which had been classed as a passive metal without any very extensive work having been done upon it (see the work of Nickle, Cohen, Osaka, Müller, Spitzer, and Hollis).

The results obtained led to similar work on iron and these in turn to a few experiments upon nickel which are supplementary to the more extensive work of LeBlanc and Levi. Unfortunately, an enforced cessation of the work leaves it in a somewhat more incomplete form than could be wished.

Method Employed.—The experiments were performed as follows:

The metals used were obtained in plate form, and cut in pieces 3 × 4 cm. with a small projection on one end, to which was sealed the copper conducting wire.

The anode was suspended in a porous cup 5 cm. in diameter and with a capacity of 100 cc. The cup was placed in a porcelain beaker and both beaker and cup nearly filled with the various electrolytes. The clay cups were thoroughly boiled in distilled water and dried after each experiment. The cathodes were two platinum plates of the same size as the anode and were hung parallel to, and at equal distances from, it on the outside of the porous cup.

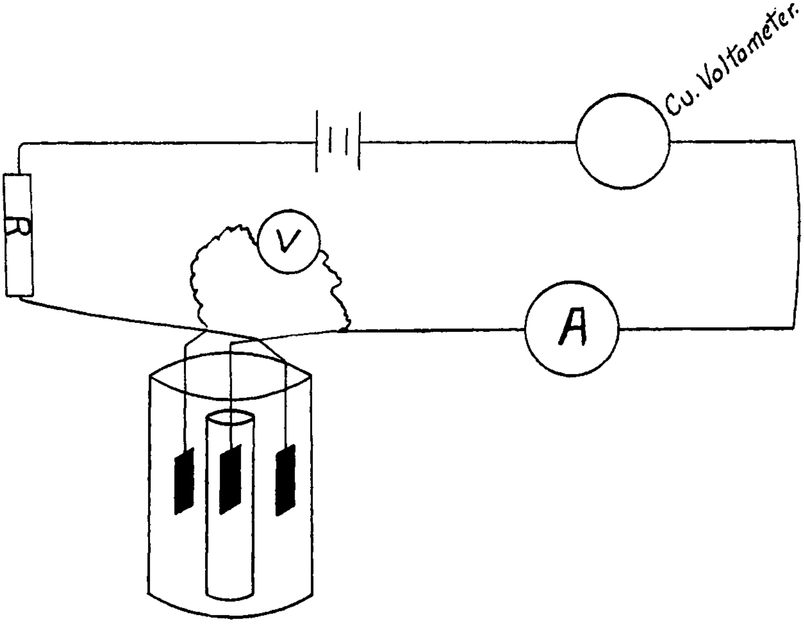
The current used was furnished by accumulators and was measured by means of an ammeter graduated to 0.01 of an ampere. When very small currents were used the time of the experiment was taken and the current calculated from the copper deposited in the voltameter.

The amount of solution from the anode was measured by the loss of weight of the anode during the passage of the current. It is expressed in the percentage of the amount which should be dissolved as compared with the amount of copper deposited in a copper voltameter, assuming the elements to dissolve in the bivalent condition and to obey Faraday's law.

The variations from 100 per cent. therefore show the degree of passivity. The copper voltameter was made according to Förster,[1] except that the voltameter vessel was covered by a glass plate, with a ground ring, fitting closely to the rim and sealed with paraffin; this glass cover was perforated with the necessary holes for the rubber stoppers needed to carry the cathode, anodes and inlet and outlet tubes for the purified hydrogen used in stirring.

The potential fall between the anode and cathode of my cell was measured by means of a voltameter and key in the usual manner.

The amount of current was regulated by means of a slide-wire resistance. This enabled me to keep the current constant when desired or to vary it at will without interruption. The whole very simple device will be seen by the sketch.



The cobalt used was the best obtainable from Merck and from Kahlbaum, both of which samples contained some nickel, and electrolytic cobalt prepared from nickel-free cobalt sulphate and precipitated according to the method of Perkin. No difference of behavior in the three samples could be noted.

The iron used was 0.2 mm. iron plate 'Kahlbaum.' The nickel was electrolytic nickel. The solutions used were prepared from Kahlbaum reagents. The calculations of percentage loss of anode were made from

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[1] Förster, *Elektroch. wässriger Lösungen, Leipzig,* 1905.

loss of weight of anode and gain in weight of cathode of the voltameter, using the international atomic weights for 1907.

The copper cathode was varied in size so as always to keep within the limits of from 0.01 to 0.02 ampere per 1 sq. cm. electrode surface. Each experiment was conducted for from 25 minutes to one hour and the amount of copper deposited varied from 40 to 100 milligrams.

The metallic plates were washed with water and alcohol and dried over an asbestos-covered wire screen heated by a Bunsen burner.

Cobalt.—The experiments tabulated below, Table I, were made, unless otherwise indicated, in normal solution of the electrolytes and at the temperature of the room. The numbers in brackets after each percentage value indicate the number of separate experiments of which the mean is given.

Discussion of Results.—In solutions of the halogen salts, sulphates, nitrates, chlorates, nitrites, dihydrogen phosphate, citric acid, acetic acid, sulphuric acid and nitric acid, cobalt as an anode goes quantitatively into solution. In the free acids also the metal dissolves by direct action of the acid so that the anode loss is greater than the copper equivalent. This quantitative solution of the metal is in striking contrast with the behavior of iron and of nickel. The cobalt can not be so handled as to remain passive as an anode in any of these solutions. Also, in contrast with iron and nickel, increase of current density has no effect unless very high densities are employed.

High density was secured by using a very small electrode and, since even with a current of less than one ampere the rate of solution is rapid, the area varied continually and the high current densities given are only approximate. In the case of sodium nitrate a current of 84 amperes per square decimeter was required to produce an evolution of oxygen on the anode but this evolution was accompanied by the formation of a dark brown oxide.

In sodium sulphate the current density of 40 amperes was sufficient to produce rapid alternations of passive and active states, as manifested by a vigorous evolution of oxygen and its sudden cessation. The cobalt was lustrous during the gas evolution and became dull during the active periods. Current of 10 amperes yields quantitative solution of the metal (not shown in table).

In sulphuric acid at 0° where a current of 0.5 ampere gives quantitative solution, the action of the free acid being at this temperature in normal solution practically zero, current densities of 200 and 400 amperes dissolved respectively 37.7 per cent. and 33 per cent. of the equivalent of the current used. This is, however, not partial passivity but periodic, and similar in every way to the periodic behavior of iron noted by the early observers and to the periodic phenomena studied by Ostwald in the case of chromium.

TABLE I.

Electrolyte.	Current density in amperes per sq. dcm.	Loss of anode.	Potential fall in in cell in volts.
$NaCl$	0.5	100.0(2)	1.0
$CuCl_2$	1.0	100.0(2)	0.3
KI	0.5	102.0(2)	1.9
KNO_3	1.0	100.0(2)	1.0
KNO_3 $N/10$	0.5	100.0(2)	2.4
KNO_3 $N/10$	3.3	100.0(3)	8.2
$NaNO_2$ (sat. sol.)	3.6	99.0(1)	3.6
$NaNO_3$ (sat. sol.)	8.4	See discussion..	...
HNO_3	0.5	177.0(1)	0.4
HNO_3	1000.0	See discussion.	...
KNO_2	0.5	104.0(1)	1.2
Na_2SO_4	0.5	100.0(2)	1.4
$CoSO_4$	1.0	100.0(2)	1.3
Na_2SO_4	40.0	Periodic passivity.	...
H_2SO_4 (temp. 0°)	0.5	100.0(1)	1.3
NaH_2PO_4	0.5	102.6(1)	1.6
Na_2CO_3	0.5	0.0(1)	2.5
KOH	0.8	0.0(2)	2.0
$K_2Cr_2O_7$	0.8	0.0(2)	2.1
KCN	0.5 → 0.7	84.6(1)	2.7 → 2.1
KCN	0.6 → 0.8	73.1(1)	2.6 → 2.1
KCN	0.4 → 0.6	80.4(1)	2.2 → 1.4
KCN	0.5	84.0(1)	2.2 → 1.4
KCN	0.5	77.8(1)	3.4 → 1.5
KCN	1.6	78.9(1)	3.0 → 2.2
$NaC_2H_3O_2$	0.5	30.9	3.8 → 3.1
$NaC_2H_3O_2$	0.5	22.0	3.0 → 2.9
$NaC_2H_3O_2$	0.6	53.0	3.3 → 3.1
$HC_2H_3O_2$	0.6	108.0	7.8
$NaHCO_3$	0.5	3.0	2.6
$NaHCO_3$	1.4	1.8	3.4
$(NH_4)_2C_2O_4$	0.4 → 0.7	50.6	0.7 → 1.5
$(NH_4)_2C_2O_4$	0.3 → 0.5	59.9	0.8 → 2.4
$(NH_4)_2C_2O_4$	0.3 → 0.5	71.0	0.8 → 2.4
$(NH_4)_2C_2O_4$	0.3 → 0.5	55.7	0.8 → 2.4
$(NH_4)_2C_2O_4$	0.5	62.1	0.8 → 2.4
$(NH_4)_2C_2O_4$	0.25	54.2	... → 2.5
$H_2C_2O_4$	0.3 → 0.4	33.4	1.7 → 1.9
$H_2C_2O_4$	0.6 → 0.7	7.0	2.2
$C_6H_8O_7$ (citric acid)	0.5	101.0	3.6
$KMnO_4$	0.4	0.8	3.0 → 3.2
$KClO_3$	0.5	100.0	1.8
$KClO_3$	600.0	Active.	...

In caustic potash, neutral sodium carbonates, and potassium bichromate, cobalt fails to go into solution, even to a minimal degree. When the plates which have been used in caustic potash are placed as anode in solutions in which they dissolve, the initial high potential fall indicative of passivity is observed, provided the circuit is closed by immersion of the cobalt anode. The cobalt surface remained perfectly bright during the whole time of my experiment though it is stated by Förster and Pignet[1] that a visible coating of sesquioxide is formed on cobalt by long electrolysis as an anode in KOH. It is stated in the contribution of Hollis[2] that cobalt, nickel and iron are passive in fuming nitric acid below a certain critical temperature which he fixes for iron at 100°, for nickel at 80° and for cobalt 10°.

This statement I confirmed in so far that a bit of cobalt plate dropped into nitric acid sp. gr. 1.5 at 15° dissolved with rapidity, while at 0° it reacted slowly for a short time and then action ceased. The cobalt was, however, covered with a dense coating which remained intact until the room temperature was reached, when vigorous reaction took place. It seemed possible, then, that the failure of cobalt to remain passive under conditions where iron and nickel are made active only with special precaution is due to the temperature. Therefore, the following measurements were made:

Solution.	Temp.	Current.	Pot. fall.	Anode loss.
KNO_3 $N/1$	0.0°	0.5	1.2	101.0(2)
$NaNO_2$ (sat.)	—6.0°	0.5	1.4	100.0(1)

In fuming nitric acid at 0° cobalt dissolved readily as anode. No measurement of the rate was made. Since Schönbein had observed that iron was made insoluble in ordinary nitric acid by heating, cobalt plates were heated, in one case until partially, and in the second until completely, covered with a dark stain. The following measurements were taken:

Solution.	Temperature.	Density of current.	Loss of anode.	Pot. fall.
KNO_3 $N/10$	room.	0.6	96.9%	2.4
KNO_3 $N/10$	"	0.6	90.0%	2.4

In neither case could any oxygen evolution be detected. In solutions of potassium cyanide the behavior of the cobalt anode is interesting particularly in reference to Fredenhagen's view of the cause of passivity. Constant potential fall could not be maintained and, unlike the following cases of partial solution, was greatest at the beginning of the experiment and gradually fell off, even with constant density of current, to a value which apparently indicated complete activity. Oxygen evolution takes place at first but ceases after a time. The table shows that constant

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[1] *Loc. cit.*, 717.

[2] *Loc. cit.*

anodic loss could not be secured. The initial 'passive' state can be secured repeatedly on the same plate by simply interrupting the current. The plate remains uncoated except for a brown soluble stain and minute brown spots.

In sodium acetate the same peculiar results obtained by LeBlanc and Levi for nickel were obtained with cobalt. There is, however, a striking difference; nickel dissolves, forming the normal green acetate. In the pink cobalt solution at first formed there appears after a time a brown coloration which gradually masks the pink color. This darkening appeared to begin at the anode and streamed downward through the solution. Its formation was accompanied by oxygen evolution and an increase in potential fall. The brown coloration on the plate was completely soluble.

In sodium hydrogen carbonate a most remarkable phenomenon appears. With a saturated solution the evolution of oxygen appears at once. The cobalt is apparently passive. However, after some time the color of the solution changes to a beautiful *green* which is fairly intense in spite of the small amount of cobalt present.

This green color is due to a cobaltic salt as will be shown in the next paragraph. The plate remained perfectly bright throughout and the cobalt dissolved is apparently lost during the first instant of current passage, since, if the experiment is long continued, no greater loss of the anode can be observed.

In ammonium oxalate solution the cobalt is found to go into solution quite as in the case of the acetate, with the difference that here the plate slowly covers itself with a coating of difficultly soluble oxalate. With a new, clean plate there appears, sinking from the anode, a pink solution characteristic of cobaltous salts. If the plate is examined from time to time, it is found more or less completely covered with the above-mentioned deposit of 'pinkish white' oxalate which adheres closely and can be washed off only with difficulty. During the period of formation of pink solution the potential fall remains practically constant. After a time, in one case thirty-five minutes, the potential fall *increases rapidly to a value of 2.4–2.5 volts, oxygen appears, and simultaneously spots of intense green color appear on the plate and spread throughout the whole solution.*

If a previously used plate is used to repeat the experiment the green color appears more quickly. In oxalic acid the green color appears at once. The formation of the green color in the ammonium oxalate solution appears not to affect the rate of solution; in the first experiment reported no green color was produced; during nearly the whole of the second experiment the green salt was produced. These green cobalt solutions in acetate, carbonate and oxalate were recognized as cobalti-salts and their instability when heated and the evolution of carbon dioxide on boiling the oxalate solution were taken as sufficient confirmation, in view of the work of Benedict.[1] The green cobalt salts were first observed by Classen[2] in the electrolysis of cobalt salts and have been investigated by Marshall,[3] Kehrmann,[4] Copaux[5] and Tubandt.[6]

At first thought this formation of cobaltic compounds from the anode of cobalt might seem analogous to the anodic solution of chromium as an acid, observed by Hittorf. There is also the accompanying oxygen evolution and high potential fall of the cell as in cases of true passivity. Also the quantity dissolved is in the neighborhood of two-thirds the theoretical yield for cobaltous ions.

In view, however, of the fact that the complex salts of cobaltic oxalate had been formed by electrolysis of cobalt oxalate by Classen and by Kehrmann and by oxidation by means of peroxides by Copaux and Benedict, it might easily be a secondary reaction in this case and indeed be due to ozone which, as is known, is liberated with the oxygen at the anode, the high resistance of the cell and the liberation of ozone being conditioned by the completion of the protecting layer of oxalate. That this view is the more probable was demonstrated by preparing cobalt oxalate, dissolving in excess of ammonium oxalate and passing in a current of oxygen led previously through an ozonizer. In the same way cobalt carbonate in the presence of sodium hydrogen carbonate solution was treated with ozone. In both cases the green salts were easily produced. In the case of the oxalate the complete conversion was slow in spite of an abundant supply of ozone and 0° temperature. In the case of the carbonate the transformation was more rapid and indeed, solid moist carbonate was turned completely green. It was not possible by means of ozone to produce the green solution in sulphate or nitrate of cobalt at 0°.

(Note: These interesting qualitative observations deserve a fuller investigation. I believe the formation of these compounds in this way is new as are also the solutions of the carbonate and acetate. It was also noted that on acidifying the green carbonate solution with nitric, sulphuric and hydrochloric acids the green color was not destroyed. This renders practically certain the existence of the simple cobaltic salts of which only the sulphate $Co_2(SO_4)_3.18H_2O$ has as yet been reported (see Marshall, *loc. cit.*)).

There remains only to mention that in potassium permanganate the failure to go into solution depends upon a dense, firmly adhering brown coating which does not wash off in water.

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[1] THIS JOURNAL, 26, 695 (1904), and 28, 171 (1906).

[2] *Ber.*, 14, 1622.

[3] *J. Chem. Soc.*, 59, 760 (1891).

[4] *Ber.*, 19, 3101 and 24, 2324.

[5] *Ann. chim. phys.* [8] 6, 508 and *Compt. rend.*, 134, 1214.

[6] *Z. anorg. Chem.*, 45, 73.

Iron.—The experiments on iron are so numerous that no simple table would be helpful. The results are therefore grouped and a discussion of results follows each table.

Concentrations, unless specified, are normal.

TABLE II.

No.	Electrolyte.	Temperature.	Current density.	Anode loss.	Potential fall.
1.	NaCl	Room.	0.5	100.0%	1.2
2.	$CaCl_2$ *N*/10	"	0.5	101.0	—2.8
3.	HCl	"	0.5	123.0	—0.0

In solutions of the halogen salts as well as in acids the iron dissolves quantitatively as an anode. No further experiments were deemed necessary to confirm the long-known absence of passivity under these conditions. Even with a current of 1000 amperes per square decimeter iron dissolves in sodium chloride solution and apparently quantitatively. The iron used was slowly acted upon by normal hydrochloric acid and therefore according to Kreussler (*loc. cit.*) is not pure. Kreussler states that absolutely pure iron is unacted upon by concentrated or dilute hydrochloric acid. This direct action of the acid is not prevented by a current of electricity and is responsible for the excess of solution in free acid shown in this and subsequent tables. In ferric chloride, also, the iron dissolves both by anodic solution and by direct reduction of the chloride.

TABLE III.

No.	Electrolyte.	Temp.	NO_3 anions. Current density.	Loss of anode.	Pot. fall.
1.	KNO_3 *N*/10	0.0	0.5	0.6	4.2
2.	KNO_2 *N*/10	0.0	0.5	100.0	2.2
3.	$NaNO_3$	22.0	0.5	0.0	2.9
4.	$NaNO_3$	22.0	0.5	110.0	1.0
5.	KNO_3 *N*/10	55.0–60.0	0.5	97.0	1.4
6.	KNO_3 *N*/10	60.0	0.5	101.0	1.4
7.	HNO_3	0.0	0.5	133.0	0.3
8.	HNO_3	0.2	0.5	0.3	2.3
9.	HNO_3	23.0	0.5	230.0	0.0
10.	HNO_3	23.0	0.5	0.5	2.4
11.	HNO_3	0.0	25.0	Active	...
12.	HNO_3	0.0	30.0	Passive	...
13.	HNO_3	22.0	60.0	Active	1.0
14.	HNO_3	22.0	65.0	Passive	3.0
15.	HNO_3	70.0	240.0	Periodic passivity	...
17.	$NaNO_3$	22.0	17.5	Active	1.2
18.	$NaNO_2$	22.0	20.0	Passive	3.0

In consideration of the results given in Table III attention is to be especially called to three facts. (1) The iron is either quantitatively active or entirely passive. Schönbein stated that in solutions of oxygen salts, which do not react with iron, oxygen is evolved from the anode quite independently of the method of closing the circuit, and that in all other oxygen compounds passivity results only if the circuit is closed by the immersion of the anode. As the above and subsequent experiments show, the first statement is true only when iron already in the passive state is used and the second is true only within certain limits of current density.

(2) The influence of increased temperature is known to be unfavorable to the establishment or maintenance of the passive condition. This is very well shown by this table as also by others which are to follow. The fact that the critical temperature is dependent upon the current density is also shown.

(3) The effect of the current density. In experiments 11–18 the word 'active' in the 5th column means that when iron initially active is placed in the electrolyte with the current indicated it remained in the active state at least two minutes; the word 'passive,' that it attained the passive state, as shown by oxygen evolution, the bright surface of the iron and large potential fall in the cell, in at least two minutes after closing the circuit.

It will be observed that it is more difficult to cause the iron to be passive in free nitric acid than in nitrates, also that a current density of 30 amperes is sufficient to produce it in nitric acid at 0°, 65 amperes at 22° and at 70° 240 amperes were only sufficient to produce a periodic recurrence of the passive state.

A difference in the rate of solution at 0° and at 23° in the free acid is also to be noted.

Attention may here be called also to the general truth, which is well illustrated above, that when the passive state is once established a relatively very small current is required to keep the iron passive.

The sharp rise in the potential fall in the cell when the passive state is produced corresponds to the negative potential of the electrode.

In Table IV is to be observed the passive or active condition depending upon temperature, previous condition and current density as discussed under Table III.

Special attention is called, however, to Nos. 5, 6, and 7 above, and Table II reprinted from the work of LeBlanc and Levi in the section dealing with nickel.

It will be seen that a definite current density, which does not produce the passive state at once, will do so if allowed to act for a greater length of time. The interest centers upon this because of the 'passiverung' potentials measured by Fredenhagen and by Finkelstein. It happens that

Fredenhagen has given the area of his electrodes and the current which passed through his cell. A recalculation of his data from Table VII[1] shows that he had a current density of 22.5 amperes per square decimeter and that in normal sulphuric acid at 18° passivity, with consequent rise in resistance of his cell and fall of current, was completely established in about eight minutes. This value is of the same order as those given above in experiments 8 and 9.

TABLE IV.

No.	Electrolyte.	Temp.	Current density.	Anode loss.	Pot. fall.
1.	H_2SO_4	0.0	0.5	101.4	0.7
2.	H_2SO_4	0.0	0.5	3.0	2.7
3.	H_2SO_4	20.0	0.5	106.0(2)	0.3
4.	H_2SO_4	20.0	0.5	3.1	2.7
5.	H_2SO_4	0.0	20.0	Passive in 1 min.	...
6.	H_2SO_4	0.0	15.0	" " 5 "	...
7.	H_2SO_4	0.0	13.0	" " 10 "	...
8.	H_2SO_4	20.0	25.0	112.0	1.6
9.	H_2SO_4	20.0	30.0	Passive	3.5
10.	H_2SO_4	80.0	64.0	Active	...
11.	H_2SO_4	80.0	72.0	Periodic passivity	...
12.	Na_2SO_4	18.0	0.5	98.0	1.3
13.	Na_2SO_4	18.0	0.5	1.7	3.4
14.	Na_2SO_4	62.0	0.5	104.0	1.1

My results were obtained using four accumulators with a variable resistance so that the potential is unknown but it was certainly over 1 volt during the time that iron remained continuously active. The variation in current density was secured by altering the size of the iron electrode.

A study of Fredenhagen's other results reveals the like situation in all. The above experiments and those of LeBlanc and Levi lead, then, to the suspicion that the 'passiverung' potentials are really incidental to the current density, and any conclusions based upon them are not founded upon fact.

My experiments were concluded before the appearance of Fredenhagen's paper and it was impossible to make a closer criticism of the results.

It is to be observed that the work of LeBlanc and Byers (*loc. cit.*) on tungsten shows the same phenomenon of the production of the passive state by sufficient current density and, at densities below this value, the maintenance of either passive or active states according to the method of closing the circuit or other previous treatment of the anode.

In phosphoric acid we find again the same general demonstration as in Tables III and IV. Here we have the iron remaining passive, if once

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[1] *Z. physik. Chem.*, **63**, 28.

rendered so, at currents of very slight density. We also find that it takes a very much smaller current to make iron passive in phosphoric acid than in sulphuric or nitric acid. It would not seem that this should be the case were the passive condition due to anodic pressure of oxygen. At 75° the current of 20 amperes produced rapidly alternating passive and active states before the iron finally became permanently passive.

TABLE V.—SOLUTION NORMAL PHOSPHORIC ACID.

No.	Temp.	Current density.	Anode loss.	Pot. fall.
1	0.0	0.5	2.0	3.1
2	0.0	0.25	101.6	0.8
3	0.0	20.0	1.1	6.6
4	15.0	0.25	103.7	0.8
5	15.0	0.12	5.1	2.1
6	19.0	0.5	104.5	1.3
7	20.0	2.0	101.5	3.6
8	20.0	14.0	3.3	7.1
9	24.0	14.0	3.7	7.1
10	0.0	5.0	Passive	4.4
11	0.0	2.0	Active	2.2
12	0.0	1.5	Active	1.5
13	0.0	0.5	Initially passive	2.7
14	25.0	5.0	Active	2.2
15	25.0	10.0	Passive	...
16	70.0	15.0	Passive	...
17	70.0	5.0	Active	...
18	75.0	15.0	Active	...
19	75.0	20.0	Passive	...

At 70° while a current of 15 amperes made the iron passive a current of 3.5 kept it in that condition. With smaller currents the passivity disappeared.

At 25° a current of 0.12 ampere was sufficient to keep the iron passive if once made so.

TABLE VI.

No.	Solution.	Temp.	Current density.	Anode loss.	Potential fall.
1.	$H_2C_2O_4$	18.0	0.5	56.0	2.4
2.	$H_2C_2O_4$	60–65	0.5	58.8	1.1
3.	$H_2C_2O_4$	75–80	0.5	49.9	1.1
4.	$(NH_4)_2C_2O_4$	19.0	0.5	14.8	2.7–2.8
5.	$NaC_2H_3O_2$	20.0	0.5	68.0	3.6 ⟶ 4.2
6.	$NaC_2H_3O_2$	18.0	0.5	52.7	3.2 ⟶ ...
7.	$NaC_2H_3O_2$	18.0	2.8	87.0	1.8 ⟶ ...
8.	$NaC_2H_3O_2$	0.0	0.5	56.4	3.6 ⟶ ...
9.	$NaC_2H_3O_2$	0.0	6.0	95.0	8.4 ⟶ 4.4
10.	$NaC_2H_3O_2$	70–75	0.5	103.0	1.8 ⟶ 1.6
11.	$NaC_2H_3O_2$	70–75	0.5	41.6	2.9 ⟶ 2.0

The behavior of iron with oxalate and acetate anions is confusing. We have both the possibility of the passive state and the certainty of a protective coating formed by the deposition of ferrous oxalate in the oxalic acid. In the acetate the influence of the closely adhering yellow coating, which covered the plate completely in some cases and in others only partially, is very marked. In Nos. 10 and 11 in Table VI the only apparent difference is in the deposition of the coating. Where the current is large, as in Nos. 7 and 9, the rapid solution of the metal apparently prevents the establishment of a uniform coating. In no case does the protective layer wholly prevent the solution of the iron. In Experiment No. 1 the iron was apparently passive.

Efforts to maintain iron in the active condition in potassium hydroxide and bichromate were without results. The iron remained lustrous and without any evidence of an external layer.

In potassium cyanide, on the other hand, the iron is covered with a closely adherent layer, which is iridescent. Sodium hydrogen carbonate presents an interesting variation. If the iron is initially passive, it remains bright and absolutely without change in weight. If, on the other hand, it is placed in the solution and the current then passed, it behaves as the oxalate and acetate and covers itself with closely adhering ferrous carbonate.

TABLE VII.

No.	Electrolyte.	Temp.	Current density.	Anode loss.	Pot. fall.
1.	KOH	Room.	0.5	0.0	2.0
2.	KOH	75–80	0.5	0.0	1.8
3.	$K_2Cr_2O_7$ *N*/10	Room.	0.5	0.0	7.2
4.	KCN	21.0	0.5	0.2	$3.3 \longrightarrow 2.6$
5.	KCN	21.0	0.5	0.3	2.4
6.	$NaHCO_3$	22.0	0.5	0.0	2.5
7.	$NaHCO_3$	23.0	0.5	55.6	$1.7 \longrightarrow 2.0$
8.	$C_6N_8O_7$ (citric acid)	22.0	0.5	102.4	3.0
9.	$C_6H_8O_7$	24.0	0.5	43.9	4.8
10.	$C_6H_8O_7$	24.0	0.9	Active	3.0
11.	$C_6H_8O_7$	24.0	0.9	Passive (initially)	3.6
12.	$C_6H_8O_7$	24.0	2.4	Passive	...
13.	$KMnO_4$ *N*/10	23.0	0.5	0.0	4.0
14.	$KMnO_4$ *N*/10	23.0	0.2	94.0	$0.6 \longrightarrow 1.4$
15.	$NaClO_3$	15.0	0.5	0.0	3.3
16.	$NaClO_3$	15.0	0.5	143.0	1.5
17.	$NaClO_3$	15.0	0.5	0.0	3.4
18.	$NaClO_3$	15.0	0.5	130.0	1.5

In citric acid the iron may be made passive or active. As shown in

No. 9 of Table VII, if introduced in the passive state with a current of 0.5 ampere, it slowly loses its passivity. The oxygen ceases to develop and the dull appearance characteristic of the active state spreads slowly over the plate. If the current is 0.9 ampere this loss of passivity does not occur.

A current of 2.4 amperes is, on the other hand, capable of producing the passive condition. The close approach of the two limits in this case is very unusual.

Potassium permanganate and sodium chlorate are both striking illustrations that oxidizing agents are not the sole prerequisite of the passive condition.

When iron is introduced into these solutions in the passive condition, or the circuit is closed by the anode, it remains perfectly bright, but if the iron is made active and the circuit closed it not only dissolves but is violently oxidized as well. The rust washes off in the case of the chlorate. In the permanganate it is black and adheres firmly so that the value given in No. 14 is only approximate.

Nickel.—I take this opportunity to republish two tables of results given in the paper of LeBlanc and Levi partly in the interest of a symmetrical presentation and partly to facilitate comparison with the foregoing results with cobalt and iron. I add a few experiments of my own and a brief discussion.

TABLE VIII.—(BOLTZMANN'S FESTSCHRIFT, p. 185).

Electrolyte.	D_A (Amp./q. dcm.)	Elektrodenverlust in Proz.	Klemmspannung in volt.
$NaCl$	0.5	100.0	2.1
$CuCl_2$	0.5	100.0	1.1
$NaClO_3$	0.5	8.0	4.2
$NaNO_3$	0.5	5.0	3.15
$Ba(NO_3)_2$	0.5	0.0	4.5
$Cu(NO_3)_2$	0.5	1.0	2.7
Na_2SO_4	0.5	2.0	3.6
$(NH_4)_2SO_4$	0.5	2.0	3.2
$MgSO_4$	0.5	3.0	3.8
$NiSO_4$	0.5	2.0	3.6
Na_2CO_3	0.5	0.0	3.8
KOH	0.5	0.0	2.15
$(NH_4)_2C_2O_4$	0.5	7.0	2.8
$NaC_2H_3O_2$	0.5	45.0	4.6
$NaC_2H_3O_2$	0.42	63.0	4.8
$NaC_2H_3O_2$	0.32	42.0	4.1
$HgCl_2$	0.15	101.0	7.7
KCN (2N)	0.75	100.0	1.0
H_2SO_4 (N)	1.0	100.0	0.5
KI	0.5	101.0	3.2
KBr	0.5	102.0	2.9

All the above experiments, except where noted, are made in 1.5 per cent. solution of the electrolyte.

TABLE IX.—(BOLTZMANN'S FESTSCHRIFT, p. 189).

Electrolyte.	D_A (Amp./q. dcm.)	Proz. Ni gelöst.	Klemmspannung.
2*N* KCN	0.75	100.0	1.1
"	4.7	64.0	2.6
N H_2SO_4	1.0	100.0	0.5
"	1.88	100.0	0.9
"	2.8	99.0	1.0
"	3.3	88.0	1.0 → 2.5
"	3.7	69.0	1.0 → 2.6
"	5.4	12.0	1.2 → 2.7
"	7.4	4.5	2.6
"	8.7	3.5	2.7
1.5 Proz. Na_2SO_4 (bei 80°)	0.5	100.0	2.4
1.5° " " " "	3.5	90.0	6.1
1.5 " " " "	5.0	58.0	7.4

"In den Versuchen mit $D_A = 3.3–5.4$ in *N* H_2SO_4 vollzog sich der Anstieg der Spannung nicht allmählich sondern, nach einiger Minuten Versuchsdauer, plötzlich."

TABLE X.

	Electrolyte.	Temp.	Current density.	Anode loss.	Pot. fall.
1.	Na_2SO_4	Room.	0.4	74.8	1.5 → 2.5
2.	Na_2SO_4	"	0.4	100.0	1.5
3.	Na_2SO_4	"	0.5	2.0	3.6
4.	H_2SO_4	"	0.8	94.0	2.0
5.	KNO_3	"	0.5	5.1	3.0
6.	$NaNO_3$	"	0.12	Active → Passive	1.1 → 3.0
7.	$NaC_2H_3O_2$	"	0.5	3.4	3.0 → 2.8

The experiments by LeBlanc and Levi show apparently that nickel is always passive in solutions of sulphates and nitrates. This not being analogous to the behavior of either iron or cobalt, I made experiments to see if such were really the case. Experiments 1 and 2 show that it is not and No. 1 shows also that 0.4 ampere is sufficient to render nickel passive, for after half an hour the potential fall in the cell rose to the value 2.5 and oxygen was evolved. Experiment No. 4 shows nickel to be apparently in the active condition but it was introduced into sulphuric acid as the connecting link of the circuit and oxygen is evolved from its surface. Yet it dissolves in nearly quantitative proportions. In sodium nitrate a current of very small value is sufficient to make the nickel passive, yet it may be kept in the active state for several minutes with very small currents, and nickel solution is formed. In sodium acetate, ammonium oxalate or sodium carbonate, nickel does not form the red nickelic salt corresponding to the green cobaltic salt, but otherwise conducts itself as cobalt does. The experiments given in Table IX show precisely the same effect of current density as observed in the case of iron.

In general it may be seen that the passive state of nickel is more easily produced and less easily destroyed than that of iron and cobalt.

Summary and Conclusions.

The behavior of the three metals under consideration is so varied and involved as to render any brief summary of the results well-nigh impossible. The following points may be mentioned by way of emphasis:

(1) If these metals are really passive under anodic conditions, *i. e.*, show an unchanged surface, high potential fall in the cell and liberation of oxygen, they fail to dissolve to any extent. The small percentage losses given in the tables are rather to be ascribed to initial activity of the metal.

(2) When a visible change in the anode surface takes place we are usually dealing with quantitative or partial anodic solution. In case the surface is covered by a visible deposit the experiments show that passive conditions are not a necessary consequence but that in certain cases solution of the metal may still continue.

(3) None of these metals can be rendered passive in the halogen acids or their salts.

(4) In the oxygen electrolytes passivity may or may not occur; depending upon the current density, the temperature, and the treatment of the metal as well as upon the electrolyte itself. The metals may be either passive or active under exactly the same current conditions, so long as the current density is below a critical value.

(5) The current density required to produce passivity varies within wide limits and in a given electrolyte time will to a certain degree replace current strength.

(6) Many conflicting and perplexing results are obtained, *e. g.*, the behavior of all three of the metals in acetate solutions is the same yet it can not with certainty be ascribed to a protecting layer of insoluble material. The experiments fail to show certainly whether iron is passive in potassium cyanide or is simply isolated from it by a conducting layer of cyanide, etc.

(7) Interesting results in connection with cobaltic compounds are foreshadowed.

(8) Many of the results are very difficult to reconcile with Fredenhagen's explanation of the nature of passivity.

(9) No evidence is produced in favor of the valence hypothesis of Finkelstein and of Müller.

From a study of the literature in the light of my experiments I reach the following conclusions:

(1) The Faraday view of passivity, as crystallized by Beetz and Wiedemann is no longer tenable.

(2) The valency hypotheses of Finkelstein and of Müller are not yet

demonstrated to be true or false but in their present forms are unsatisfactory.

(3) The hypothesis of Fredenhagen, so far as it relates to anodic oxygen or an oxygen alloy as the immediate cause of passivity, is not to be reconciled with facts.

(4) No explanation of the phenomena of passivity even approximately satisfactory has yet been produced. I have none to offer. Yet, when the experimental development warrants it, I confidently expect the cause of passivity to be found in an altered state of the *metal itself*, this alteration, whatever its character, being produced by *any one of a number* of different agencies.

In conclusion, I wish gratefully to acknowledge my indebtedness to Prof. Max LeBlanc, of the University of Leipzig, in whose laboratory this research was carried out, for his constant helpful counsel and uniform kindness during the progress of the work. I am also grateful for the courtesies and help bestowed by Dr. Böttger. Dr. Freundlich and Dr. Drucker, Privat-Dozenten in the University.

UNIVERSITY OF WASHINGTON,
July 1, 1908.

THE VELOCITY OF REACTIONS IN GASES MOVING THROUGH HEATED VESSELS AND THE EFFECT OF CONVECTION AND DIFFUSION.

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Received September 5, 1908.

Many of the investigations of the past few years, on the velocity of reactions in gases, have been based upon the determination of the change in the composition of the gases while passing through heated tubes. The velocity coefficient has then usually been calculated by applying the formulas derived for reactions taking place in stationary gases.

Bodenstein and Wolgast[1] recently pointed out that this method of calculation is justifiable only when the gases pass through the tube entirely without mixing. For those cases where diffusion or convection has caused even partial mixing of the gases in the tube, they show that the usual method may lead to serious error. They develop formulas which hold when the mixing of the gases can be considered complete.

We have then at our disposal, for the calculation of velocity coefficients, two formulas, one of which holds when there is no mixing and the other when there is complete mixing. The only means, however, for determining which of the two formulas will give the most accurate results, in any series of experiments, is to calculate the coefficients by both formulas and then to choose that which gives the "better constant." That this method

[1] *Z. phys. Chem.*, 61, 422–436 (1908).