the silver halide had appeared in the solution, it was coagulated by the stirring, and in such form it dissolves too slowly for electrolytic decomposition to be practicable.

In spite of the unusual technique of the method, this procedure has been found to compare favorably with other gravimetric methods, both as to accuracy and speed. However, it must be confessed that this work was undertaken not so much for the purpose of developing a new method as for the confirmation of certain inferences drawn from the results of my study of electrode potentials.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

PASSIVITY OF COBALT.

BY HORACE G. BYERS AND CURTIS W. THING.

Received June 5, 1919.

Introduction.

In a paper by one of us[1] a report is given on a series of experiments on the passivity of cobalt and the following statement is made: "In solutions of the halogen salts, sulfates, nitrates, chlorates, nitrites, dihydrogen phosphate, citric acid, acetic acid, sulfuric 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. In caustic potash, neutral sodium carbonate, 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 anodes 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." 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 at 10°. In view of this contradictory behavior of cobalt and the difference between its behavior and that of iron and nickel it seemed worth while to make a further study of the topic. The experimental work detailed below is divided into 3 parts: (1) a study of the anodic behavior of cobalt in various solutions with change in concentration using small current density, (2) a study of the relation between the current density and the voltage drop across a platinum-cobalt cell using various solutions, and a comparison with similar cells using iron and nickel, and (3) a study of the anodic potentials of cobalt, iron and nickel.

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[1] THIS JOURNAL, 30, 1728 (1908).

[2] *Trans. Camb. Phil. Soc.*, 12, 462 (1904).

I.

The pure cobalt, in plate form of known area, was fastened to a copper conducting wire. This was, in turn, fastened in a glass tube and sealing wax applied so that the electrolyte came in contact with the cobalt only. The whole was suspended in a porous cup within a beaker and both were filled with the electrolyte. The cathodes used were two platinum wires, sealed through glass tubes, and were hung parallel to and at equal distances from the anode, on the outside of the porous cup. The cup served to keep the cobalt anode unaffected by the hydrogen from the cathodes. The two cathodes gave a more uniform current density on the anode. The temperature used in all measurements was 0°.

The amount of solution from the anode was measured from the loss in weight of the anode during the passage of the current. From the copper deposited in a copper coulometer the amount of cobalt which would have dissolved, assuming the metal to dissolve in the bivalent condition and to conform to Faraday's laws, may be calculated. Comparing the amount actually dissolved to the amount which theoretically should dissolve, the degree of passivity was calculated.

Except where otherwise indicated, the cobalt used was prepared electrolytically from nickel-free cobalt sulfate. A part of the work was done with Merck's 98% cobalt. No difference between the behavior of the two samples could be detected.

A. Nitric acid solutions of normality 0.01 to 5.0 were used. The current densities employed varied from 3.0 to 0.1 amp. per sq. dcm.

B. Sulfuric acid solutions of normality 0.02 to 5.0 were used. The current densities employed varied from 0.1 to 2.7 amp. per sq. dcm. With these current densities the cobalt was active. In every case the cobalt went into solution in accord with Faraday's law plus an amount varying between 9 and 110%, due to the solvent effect of the acid. The metal was evidently active.

It was afterwards found that in a 0.2 *N* solution, if the current density was increased to 16–17 amp. per sq. dcm. and then reduced to the densities noted in Table I, that the cobalt would be passive. This is shown in the following table:

TABLE I.—98% COBALT IN 0.2 *N* SULFURIC ACID AT 0°.

Area anode. Sq. cm.	Current. Mil. amp.	Loss of anode. G.	Gain of copper. G.	Current density. Amp. per sq. dcm.	% loss of anode.
0.256	10	0.0100	0.0105	3.92	100.3
0.330	15	0.0151	0.0158	5.0	102.0
0.272	15	0.0004	0.0187	5.5	2.3
0.322	15	0.0002	0.0207	4.6	1.0

In the first two cases the initial high density was not employed and the cobalt was active. In the last two cases the initial high current density of 16–17 amp. per sq. dcm. rendered the cobalt passive and it remained passive even at the low current densities of 5.5 and 4.6 amp. per sq. dcm. The small loss was due to the initial period of activity and to mechanical losses during the cleaning and weighing of the electrode.

C. Sodium sulfate solutions of normality 0.01 to 5.0 were used. At small current densities the cobalt was active. Using 0.2 *N* solution, it was found that cobalt would become passive providing a sufficiently high current density as employed.

D. In potassium dichromate solutions of all concentrations and at all current densities cobalt remained passive. It was found that additions of small amounts of sulfuric acid or sodium sulfate solutions would render the cobalt active.

Summary.—In 0.2 *N* sulfuric acid and sodium sulfate solutions, cobalt may be either active or passive at 0° dependent upon the current density. In potassium dichromate it readily assumes the passive state under all conditions. The passive state is not so readily reached in the presence of activating agents.

II.

A cell containing the electrolyte, having an anode of known area and a platinum foil cathode, was placed in series with a milliammeter. A voltmeter was connected across the two electrodes by means of a key. In series with the cell and ammeter was a variable resistance. A direct current of 15 volts was used.

The voltage fall across the cell was gradually increased. Readings of the voltage and current were made. At a certain point the voltage fall suddenly increased while the current simultaneously decreased. At the same time the surface of the anode brightened and bubbles of oxygen gas were evolved. This marks the change of the metal from the active to the passive state. The following curves in Fig. 1 show the results for 99.7% iron, 100% nickel, 98% cobalt, and 100% cobalt. Solutions of 0.2 *N* sulfuric acid, sodium sulfate, and potassium dichromate were used. The temperature was 0°. The following table gives the area of the respective anodes:

TABLE II.—AREA OF ANODES IN SQ. CM.

Metal.	0.2 *N* H_2SO_4.	0.2 *N* Na_2SO_4.	0.2 *N* $K_2Cr_2O_7$.
Iron (99.7%)	0.201	0.066	0.068
Nickel (100%)	0.120	0.068	0.068
Cobalt (98%)	0.087	0.085	0.168
Cobalt (100%)	0.15	0.045	0.045

From an inspection of these curves and by calculations it may be seen that nickel is passive in all the solutions and at all current densities.

Iron is passive at all current densities in potassium dichromate and sodium sulfate, and becomes passive at current densities above 6.0 amp. per sq. dcm. in 0.2 *N* sulfuric acid.

Cobalt becomes passive in 0.5 N sulfuric acid at 16–17 amp. per sq. dcm., in 0.2 N sodium sulfate at 24 amp. per sq. dcm. It is passive at all times in 0.2 N potassium dichromate.

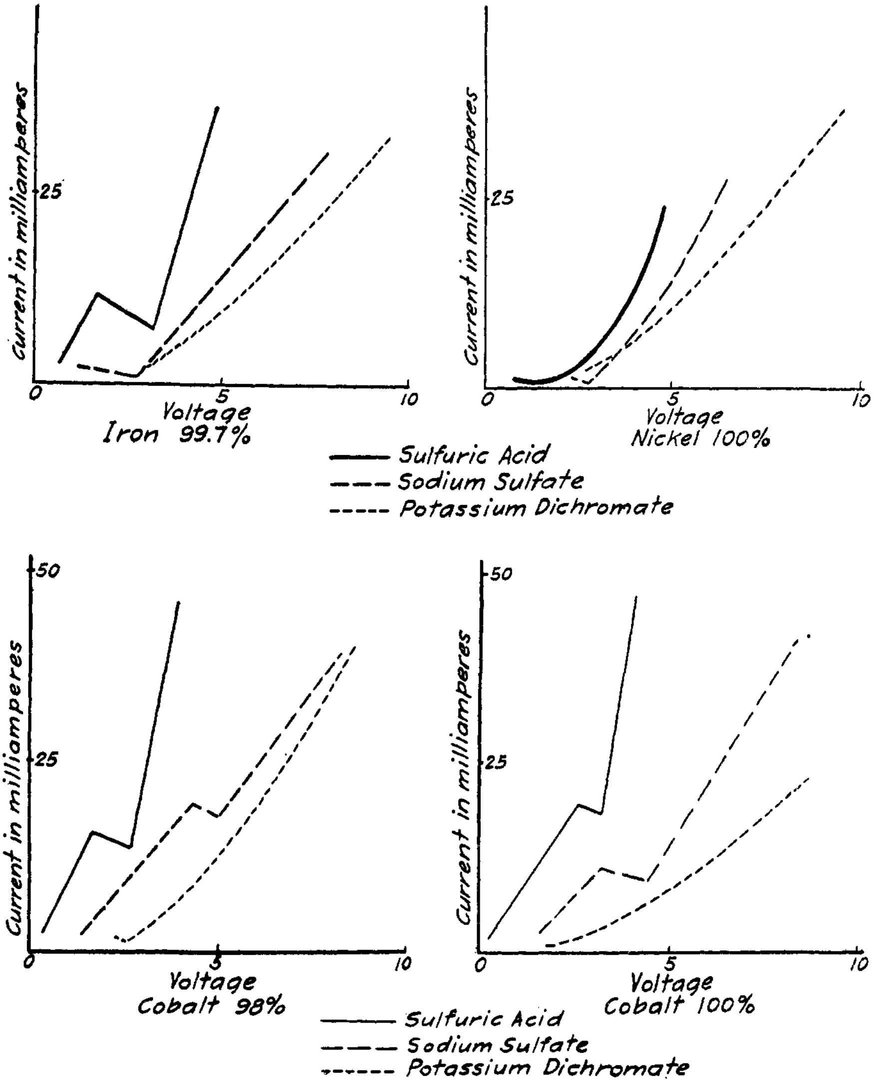

Fig. 1.

The above curves represent average experiments and values may be obtained which will differ slightly from those given. The time factor influences results. By this we mean that if the current density were somewhat lower than the above values, and the current were allowed to flow for a longer period of time, the metal would become passive. For example, cobalt in 0.2 N sulfuric acid will become passive at a current density of 10 amp. per. sq. dcm. if the current is passed for a sufficient length of time.[1]

Summary.—Cobalt as an anode becomes passive if the current density is of a sufficiently high value. The passive state is indicated by an increased voltage drop, a decreased current, by the evolution of oxygen gas, and by the failure of the anode to go into solution.

III.

In this series of experiments, the potential of the anode was measured against that of a normal calomel electrode as zero. The potential was measured when no current was flowing and also when the anode was a part of a platinum-metal cell using various electrolytes. The potentiometer used was a Leeds and Northrup student potentiometer and measured voltage to the fourth decimal place. Owing to the nature of the work readings were made to the third place only. A Weston standard cell was used with the potentiometer. All measurements were made at 0°. The electrolyte was contained in a large test-tube. The anode was prepared by fastening the metal, either in the wire form or as a narrow strip, to a copper wire. This was sealed through a glass tube with sealing wax so that the metal only came in contact with the electrolyte. A platinum foil cathode was used. The calomel electrode was prepared in the usual manner and checked from time to time against amalgamated zinc in molar zinc sulfate, a voltage of 1.03 being obtained.

Metal.	Active potential. No current.	Potential. Current flowing.	State of metal. Current flowing.
A.—0.2 N Sulfuric Acid AT 0°.			
Iron (99.7%).......	—0.514	+1.911-1.887(10)[a]	Passive
Nickel (100%)......	—0.234	1.916-1.902(5)	Passive
Cobalt (98%)[b]......	—0.350	0.605-671(15)	Active
Cobalt (98%).......	—0.278	1.888-1.849(15)	Passive
B.—0.2 N Sodium Sulfate at 0°.			
Iron (99.7%).......	—0.616	1.959-1.971(5)[a]	Passive
Nickel (100%)......	—0.167	1.809-1.797(5)	Passive
Cobalt (98%)[b]......	—0.411	0.270-0.250(5)	Active
Cobalt (98%).......	—0.411	1.811-1.824(5)	Passive
Cobalt (100%)[b].....	—0.416	0.302-0.264(5)	Active
Cobalt (100%)......	—0.416	1.870-1.840(5)	Passive
C.—0.2 N Potassium Dichromate at 0°.			
Iron (99.7%).......	—0.185	2.634-2.592(5)	Passive
Nickel (100%)......	—0.400	2.268-2.290(5)	Passive
Cobalt (100%)......	—0.306	2.422-2.522(5)	Passive

[a] Was not subjected to the initial high current to secure the passive state.

[b] The figures in parenthesis indicate the current in milliamperes flowing through the anode.

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[1] See THIS JOURNAL, 35, 767 (1913); 36, 2004 (1914).

The electrode was immersed in the electrolyte and its potential determined with no current flowing. Then a current of 50 milliamperes was allowed to flow through the anode until it became passive. The current was then reduced and the potential again measured. The current was allowed to flow for a long period of time and then the electrode was removed and the loss in weight checked against the copper equivalent from the copper coulometer. It seems to be impossible to get exact potential checks. This is due probably to variations in the electrode surface and in the current employed. It was found that fluctuations in the current very materially affected the potential The summary of the results obtained is shown in the preceding table.

The above results show (1) the metals in the active state possess a negative potential. Experiments show that this potential will vary with time[1] and with the material and surface of the cathode; (2) the potential of the anode when passive is positive and likewise varies with time. It was also found that the potential of the anode varied with the current flowing through it. For example, in 0.2 *N* potassium dichromate, the same passive cobalt anode will show a potential of 1.920 with a current of 5 milliamperes and a potential of 2.40 with a current of 10 milliamperes.

Summary.—A series of measurements of the anodic potentials of iron, nickel, and cobalt are given. From an inspection of the results it may be seen that when in the active condition and no current is flowing through the electrode, it has a negative potential. When the electrode is an anode with the current flowing, the potential changes in sign and increases in value even if the metal remains active. If, however, the metal becomes passive, the potential is markedly increased.

Conclusions.

The results of experiments show that, at low current densities, cobalt, when used as an anode, readily goes into solution. If the current densities are sufficiently high, the cobalt becomes passive and is insoluble. The voltage measurement of the cobalt-platinum cell, with various electrolytes and a comparison with similar results with iron and nickel, show that when the cobalt becomes passive there is a marked increase in the voltage across the cell. It may be seen from the potential measurements that this is due to the change in potential of the cobalt as it changes from the active to the positive state.

Cobalt may be classed with the passive metals since it exhibits all the characteristics of iron and nickel when they are passive. The essential difference between the cobalt and the other metals lies in the fact that the cobalt as an anode will not become passive at the low current densities required by nickel and iron. If cobalt assumes the passive state, it will remain so even though the current density is reduced. In the absence

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[1] See also THIS JOURNAL, **38**, 363 (1916).

of the anodic relation, the cobalt becomes active in acid solution more readily than does nickel.

SEATTLE, WASHINGTON.

THE RAPID DETERMINATION OF CARBON MONOXIDE IN AIR.[1]

BY ARTHUR B. LAMB AND ALFRED T. LARSON.

Received June 28, 1919.

The breathing of air containing 1% of carbon monoxide by men in moderate activity will lead to loss of consciousness within a few minutes, followed very soon by death. 0.1% of carbon monoxide may cause disablement in about 2 hours and 0.05% is sufficient to induce drowsiness on prolonged breathing.

The testing of the efficiency of gas mask absorbents for carbon monoxide, therefore, involves the precise analysis of air mixtures containing 1% and less of this gas. Moreover, to follow adequately the behavior of an absorbent during a test, frequent and very rapid analyses are required.

When testing of this nature became necessary in the Research Division of Chemical Warfare Service, a search for a satisfactory method was made, but none was found at once sufficiently accurate and rapid for this purpose.

Methods depending upon absorption, such as the cuprous chloride and the Haldane methods, were out of the question, since the volume changes to be measured at these concentrations were so minute. Conversion to carbon dioxide and its determination was not suitable because of the difficulty of securing rapid and at the same time complete absorption of carbon dioxide at very low concentrations. The liberation of iodine from iodine pentoxide furnished a very accurate method, particularly at concentrations of carbon monoxide as low as 0.1%, but it was found to be time consuming.

Thermometric methods depending on the rise of temperature produced by the combustion of the carbon monoxide had, to be sure, been described, particularly in the patent literature, and they had, at least, the merit of rapidity. Thus, Guasco[2] had proposed a differential air thermometer in which one of the bulbs was of platinum covered with platinum black. The device has been found to poison rapidly, requires frequent calibration, and is not accurate at low concentrations.

A. and L. D. Williams[3] had described an arrangement which employs

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[1] Published by permission of Maj. Gen. W. L. Sibert, Director of Chemical Warfare Service, U. S. A.

[2] *Compt. rend.*, 155, 282 (1912).

[3] U. S. pat. 1,143,473. June, 1915.