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Electrode potential of galena

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ELECTRODE POTENTIAL OF GALENA.

by

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A

THESIS

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Professor of Chemistry.

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ELECTRODE POTENTIAL OF GALENA.

W. Skey, in 1870, found that various sulphide minerals were capable of forming the negative pole of a galvanic cell when treated with sulphuric acid* Forty years later V. H. Gottschalk and H. A. Buehler showed that a battery was formed and an electric current produced when various sulphides were treated with water only**. The authors arranged a number of the minerals in a series according to the electromotive force measured against copper, using distilled water as the electrolyte, and discussed the probable bearing of this as a factor in the leaching and subsequent enrichment of ore deposits.

The work of Skey, above quoted, was done without any measureing instruments: although his paper gives but little experimental detail, the electrolytic behavior of minerals is demonstrated and the existence of an electrolytic potential at the contact of conducting mineral and liquids is proved beyond question: for example, the relative order of the electrode potentials is estimated by

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*Skey, W.: Transactions and Proceedings of the New Zealand Institute; vol.III, 1870, pp.222-236.

**Gottschalk, V. H., and Buehler, H. A.: The Economic Geologist, vol.VII, No.1, p.15, (1912).

actually using the minerals as electrodes of a battery, the direction of the current being given by the electrodeposition of gold in a second vessel: this ocular evidence is non-controvertible as well as striking and the advances in electrochemistry, for the past forty years have fully confirmed Skey's interpretation of the effects.

Gottschalk and Buehler were led to seek such an electrolytic effect from the ~~neutral~~ mutual action of pyrite and certain other natural sulphides on one another when placed in contact and moistened: their unpublished results include measurements of the amperage developed, electromotive force measurements, and a variety of additional cases of contact action.

It may thus be regarded as definitely established that an electric current is set up by various minerals in contact with solutions. When connected as batteries, the minerals may be suspended in the liquid by copper wire- care being taken to prevent the liquid from reaching the wire- and the electromotive force may then be measured by the Lippmann capillary electrometer. This, however, was found inconvenient, so most of the observations were taken by placing a drop of the liquid on the mineral and bringing into contact with the liquid a copper wire or a platinum wire, compensating the electromotive force by Poggendorff's method, with a Lippmann electrometer as zero-instrument.

In the present work, this method was used, chiefly with galena: the values given below (as all values given in this paper) are not absolute but merely serve as a basis for comparison. From a large number of observations, on various pieces of freshly fractured galena, using distilled water and copper wire, the extreme variations were found to be from +0.224 to +0.060 volts. With platinum, distilled water, and freshly fractured galena the values varied from -0.151 to -0.005 volts. With platinum, distilled water, and a piece of galena ~~that~~ which was somewhat weathered, the values were found to be somewhat higher and varied from -0.344 to -0.224 volts. The fact that there is always an electromotive force exerted and that it is always in the same direction for a given set of conditions would lead one to believe that by the elimination of certain factors causing irregularities one should be able to find a set of conditions that would give a constant electromotive force for any mineral.

With this end in view a normal calomel electrode (+0.560 volts) and a normal mercurous sulphate*

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*Sauer: Zeitschrift Physikalische Chemie, vol.47, p.146.

electrode $\{(+ 0.962 + 0.0011(t-18^\circ))\text{volts}\}$ were used, hoping that in this way the constancy of the electromotive force obtained would be increased. Some of the minerals were treated with a drop of the liquid used in the electrode. Later the electrode was connected to a tube containing the liquid with which the mineral was to be treated. Both the tube containing the liquid and the tube on the normal electrode were drawn to a condition of fine capillarity. However, the question of diffusion is one that cannot be ignored. Even under these conditions it was found that great irregularities existed in the values obtained.

The difficulty of assigning an absolute value to the electromotive force exerted by galena will at once be recognized by a consideration of the following, which are a few of the factors causing variations:

(A) The different faces of a crystal of galena give values which vary through rather wide limits. The irregularity of even these variations makes it uncertain as to whether they are due to the fact that the faces are different or to other factors. (See Table I.)

(B) Different spots on the same face give values which vary considerably. These values can not always be reproduced for the same spot after the water has been removed and fresh water supplied. This is especially true after the lapse of several days' time. (See Table II.)

(C) The element of time seems to be a factor of some importance. In the case of galena, platinum and sulphuric acid if a reading be taken at once and at intervals of a few minutes it will be found that the values rise gradually for sometime. With ammonium acetate, instead of sulphuric acid, it was found that the values gradually decrease with time. (See Table III.)

(D) It was also noticed that by making a circuit of the mineral, the water, and the copper, and keeping it closed for some minutes, the values of the electromotive force produced could be greatly decreased. (See Table IV.)

(E) The influence of the size of the drop on the values obtained in the case of acids, where the action is strong, is not great. However, in the case of water it is quite noticeable, the small drop giving a higher reading than if the face of the crystal be well covered. This greater value of the electromotive force may be the result of an acceleration of the action, due to surface tension. (See Table V)

(F) A rather large variation was noticed in different pieces of galena. This difference is certainly due in part to the degree of weathering which has taken place in the mineral. It is probably due, in part, to varying amounts of impurities existing in the various crystals. (See Table VI.)

With all these causes of variation existing it is probable that no definite value can be assigned to the electromotive force exerted by galena- at any rate not until a great deal more work has been done along this line.

While there is no question as to the fact that there is an electromotive force set up, when minerals are treated in this way, there is some doubt as to the reaction causing this. In order to inquire into the nature of this reaction a number of experiments were performed with various strengths of several solutions, measuring the electromotive force against platinum. Saturated solutions of potassium permanganate (neutral), sodium hydroxide, and commercial varieties of concentrated hydrochloric and nitric acids, were used. For each succeeding observation the strength of the solution was half of the previous value. (Curves showing these values will be found at end of this paper.)

While it must be remembered that the electrode potential of platinum may vary with different solutions and different strengths of the same solution, still these results show in a general way that the stronger oxidizers and the more active acids give the higher values. (Compare LeBlanc, Text-book of Electrochemistry, p.256.)

To further carry on this investigation a number of mineral batteries were set up, using galena for one electrode and pyrite or marcasite for the other. Various solutions were used as electrolytes. The results of these experiments appear at the end of this paper in tabulated form. (See Table VII.) While it is true that for similar batteries exactly the same electromotive force was not produced, yet it is true that this value is the same within less than 0.09 of a volt in every case.

During the run of these batteries, the outside circuit of each was kept closed and a reading of the electromotive force was taken at intervals for several days. This could not be long continued as the liquid in every case crept up the mineral and soon wet the contact between the mineral and the copper wire. The batteries all behaved in much the same way- except No.10A, which will be discussed later. The electromotive force began to decrease as soon as the batteries were started and continued to do so as long as they could be run. It was observed that by leaving the outside circuit open for some time the voltage increased from 0.02 to as much as 0.06 volts in every case. It will be remembered that this same effect was noticed in the case of a drop of water on the mineral except that there the electromotive force decreased when the circuit was kept closed for some little time.

Now if it is true that this electromotive force is the measure of the rate of oxidation and solution, as contended by Gottschalk and Buehler*, then one would expect to find the galena attacked and the iron disulphide remain fresh, when connected in a battery in this way. Apparently this is not what takes place. Of the pieces of galena in these batteries not one was affected while in every case the disulphide of iron showed decided signs of being attacked. The iron mineral turned a reddish yellow as far as the solution covered it and the electrolyte showed iron in solution.

In the battery, using strong sodium hydroxide solution as the electrolyte, the galena was positive to the iron disulphide. The exact cause of this is not well understood. It is known, however, that the order of deposition of galena and iron disulphide in nature is exactly opposite in the case of precipitation from acid and alkaline solutions. In all probability these two facts are re-

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Gottschalk and Buehler: Oxidation of Sulphides; 2nd paper.

lated.

In this paper it has been impossible to lead to a definite conclusion as to the cause of this electrolytic phenomenon. The object has been rather to point out some of the difficulties to be encountered in work along this line. The subject of the electrode potential of the various minerals is one offering a rich field for investigation and has a very close bearing on the oxidation and redeposition of minerals in nature.

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In the tables which follow all signs refer to the galena; figures are "volts", using the ~~Austin~~ Weston cell as 1.019 volts.

The following are observations made with copper wire, distilled water, and a cubical piece of galena.

Table I.

Face	Electromotive force		
	Max.	Min.	Ave.
1	+.075	+.060	+.068
2	+.103	+.072	+.079
3	+.157	+.154	+.156
4	+.134	+.119	+.127
6	+.134	+.083	+.109

The following observations were made with platinum wire, distalled water, and galena: (All observations were on the same face.)

Table II.

Spot	1	2	3	4	5
E.M.F.	-.048	-.024	-.005	-.045	-.018
E.M.F.	-.064	-.100	-.092	-.123	-.081

The following observations were taken with platinum wire and galena, one table being with normal sulphuric acid and the other with ammonium acetate:

Table III.

Values with $\frac{N}{1}$ H_2SO_4		Values with $NH_4(Ac)$	
E.M.F.	Time	E.M.F.	Time
-.218	At once	-.311	At once
-.254	After 1 minute	-.321	After 3 minutes
-.301	After 4 minutes	-.248	After 7 minutes
-.340	After 7 minutes	-.238	After 10 minutes
-.354	After 11 minutes		

The following observations were taken with distilled water, copper wire, and chalcopyrite:

Table IV.

Reading	Remarks
+.167	This reading taken at once.
+.105	This reading after a short circuit.
+.022	This is the limit to which it could be run down.
+.090	Reading after building up one minute.

The following observations were taken with galena, distilled water, and copper wire:

Table V.

Reading No.	Little Spot	Big Spot
1	+.078	+.078
2	+.122	+.063
3	+.150	+.131
4	+.075	+.060
5	+.157	+.154
6	+.134	+.119
7	+.134	+.083
8	+.072	+.072
9	+.103	+.069

The following observations were taken with distilled water, copper wire, and various galena specimens:

Table VI.

Specimen No.	E.M.F.
1	+.224
2	+.093
3	+.078
4	+.150
5	+.060
6	+.119

The following are the results of the experiments with batteries using galena and iron disulphide as electrodes in various electrolytes:

Table VII.

Battery Number	Electrodes Galena against	Electrolyte	At once	Next day	After leaving circuit open for 45 minutes
4	Pyrite	M.S.M.tap H_2O	-0.545	-0.114	-0.152
5	do	do	-0.288	-0.071	-0.118
1	Marcasite	do	-0.260	-0.066	-0.111
2	Pyrite	Dist. H_2O	-0.276	-0.185	-0.197
7	do	do	-0.310	-0.125	-0.161
8	do	do	-0.381	-0.125	-0.158
6	Marcasite	do	-0.254	-0.096	-0.151
6A	do	do	-0.340	-0.195	———
9	Pyrite	$\frac{N}{3}$ H_2SO_4	-0.384	-0.027	-0.043
11	do	do	-0.362	-0.004	-0.006
10	Marcasite	do	-0.332	-0.043	-0.087
10A	do	saturated sol. NaOH	+0.269	———	———

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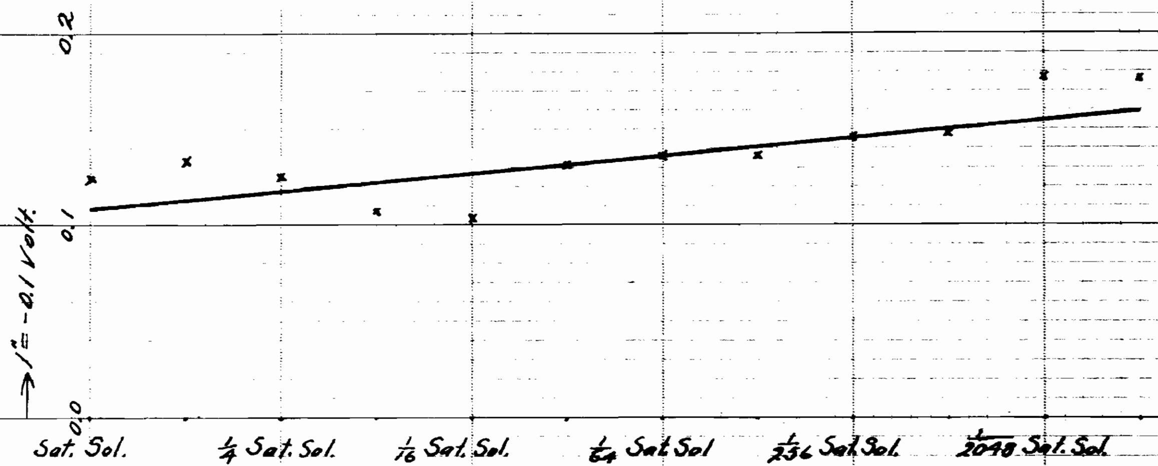
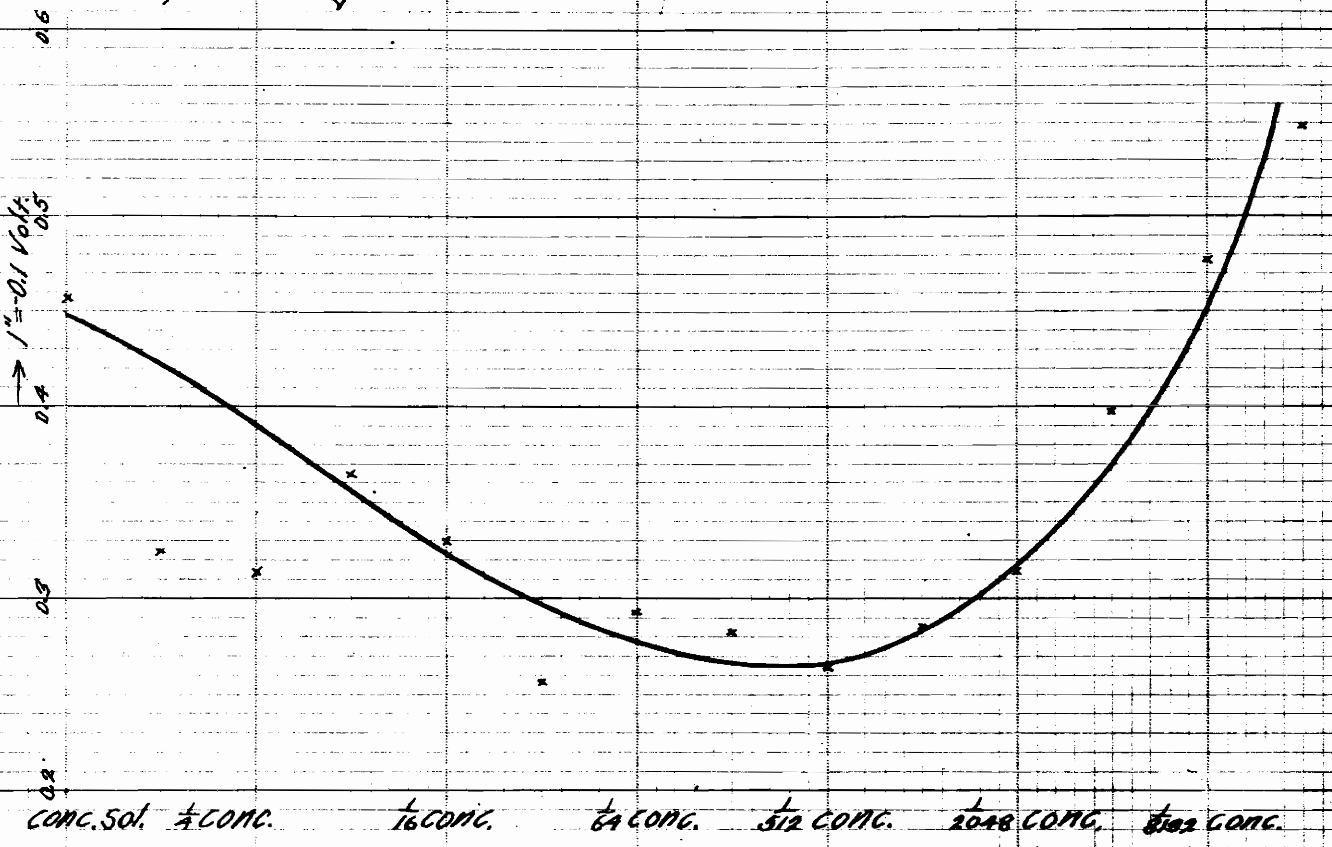
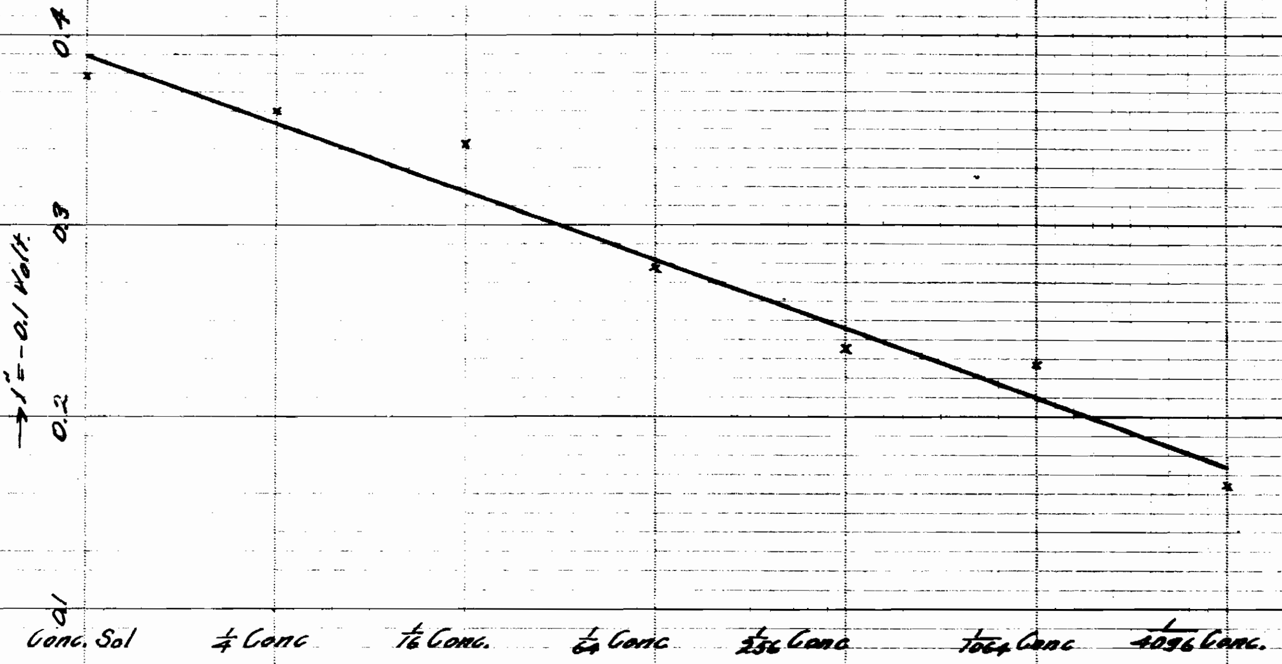
Curve of values of electromotive force of galena against platinum for various strengths of sodium hydroxide solution.

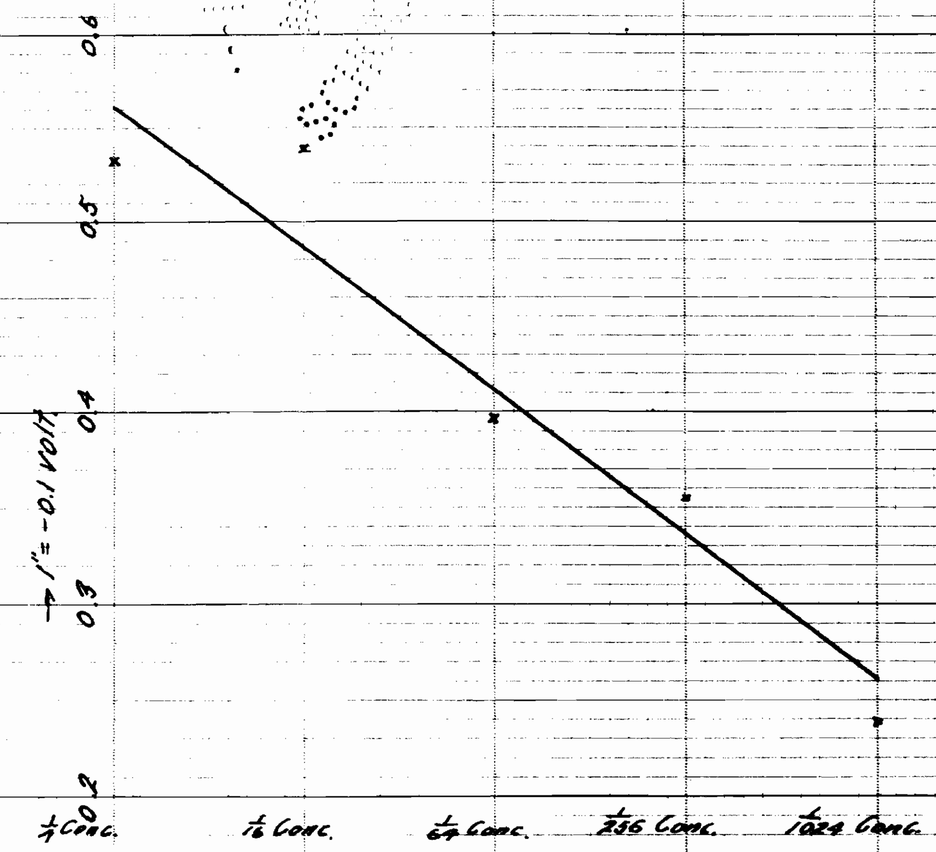


Curve of values of electro-motive force of galena against platinum, for various strengths of potassium permanganate solution.



Curve of values of electromotive force of galena against platinum for various strengths of hydrochloric acid solution.





Curve of values of electromotive force of galena against platinum for various strengths of nitric acid solution.