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Effects of the Composition of Solution on the Potential of Pyrite Electrode

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With 9 Text-figures

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I. Introductory

R. C. WELLS, well known for his investigations on the potential of several mineral electrodes, classifies the potential of pyrite electrode as either "ferric-ferrous" or "sulphide."¹⁾

The subject was thoroughly studied from a leptological point of view by Prof. A. MATSUBARA,³⁾ who came to the conclusion that the potential of pyrite electrode is proportional to the surface density of "free crystalline bond" of a surface in action, and that the electrical phenomena exhibited by pyrite are chiefly due to the action of its sulphur atoms.

Under his suggestion, the present writer made an attempt to determine the effects of hydrogen ion concentration of a solution on the potential of a sulphide mineral electrode. So far as the ex-

¹⁾ R. C. WELLS, "Electric Activity in Ore Deposits," Bulletin U. S. G. S., 548 (1914).

²⁾ A. MATSUBARA, These Momoirs, Ser. B, Vol. I, No. 4.

perimental results are concerned, it is quite possible to say that the potential of pyrite electrode can be expressed by a general equation such as

$$E = E_0 + k \log [H']$$

where E_0 denote the *k* are constants which are almost independent of the concentration but depend on the nature of the solution, and [H[·]] the hydrogen ion concentration.

II. The Potential of Pyrite against Acid and Alkaline Solutions

In order to corroborate the effects of change in the concentration of acid and alkaline solution upon the potential of pyrite, the following experiments were carried out. Sulphuric acid and sodium hydroxyde solutions of various concentrations, ranging from 6 normal to 10^{-5} normal, were respectively prepared. About 50 c.c. of each of them was placed in a glass jar having a capacity of ca. 200 c.c. The air was completely expelled from the jar by introducing a stream of knal gas through the solution for an hour or so before the measurements. For the electrode particular care was taken to select a specimen having a perfectly smooth and shining crystal face, free from all mechanical and chemical defects such as striation, tarnish and minute etched graving. The piece of pyrite thus selected was fastened to the end of a suitable glass tube by means of sealing wax, which covered the whole except the crystal face which was to serve as an electrode. It was immersed in the solution by means of a plug fitted to the mouth of the jar. This half cell was connected to a saturated potassium chloride calomel electrode¹⁾ in conjunction with a saturated salt bridge. The latter was prefered in order to eliminate or minimize the contact potential brought about by the interdiffusion at the conjunctions. The whole was kept at 18°C in a thermostat.

All measurements were made by a methode of compensation with a galvanometer of fairly high sensibility. The electromotive force of the cell underwent some change during about half an hour or so after the immersion of the electrode, but after it had settled

LOOMIS and ACREE, Amer. Chem. J., 46, 621 (1911).
 FALES and VOSBURGH, J. Amer. Chem. Soc., 40, 1291 (1918).
 FALES and MUDGE, *ibid.*, 42, 2434 (1920).

nearly to a constant, the reading was taken. The potential of pyrite electrode was obtained from the electromotive force of the combined cell and the potential of saturated potassium chloride calomel electrode, namely 0.5252 volts at 18° C¹; but the diffusion potentials were not taken into account. The following tables show the results thus obtained.

Electrodes	I (volt)	II (volt)	III (volt)	IV (volt)		
6n-H ₂ SO ₄	0.928	0.946	0.924	0.950		
n "	0.951	0.952	0.932	0.950		
10-1 ,,	0.940	0.943	0.927	0.935		
10-2 ,,	0.902	0.912	0.898	0.908		
10-3 "	0.846	0.857	0.855	0.855		
10-4 ,,	0.790	0.812	0.799	0.805		
10-5 "	0.748	0.753	0.745	0.752		
		/	,			

Table IElectrode: (100) of pyrite from Tsunatori.

Table II

Electrodes	I (volt)	II (volt)	III (volt)	IV (volt)
6n-NaOH	0.310	0.290	0.322	0.310
n ",	0.314	0.319	0.334	0.314
10-1 "	0.375	0.357	0.389	0.361
10 ⁻² "	0.432	0.402	0.424	0.404
10-3 "	0.482	0.461	0.466	0.449 *
10-4 "	0.538	0.521	0.507	0.511
10-5 "	0.580	0.596	0.600	0.573

Electrode: (100) of pyrite from Tsunatori.

The relations between the potential and the concentration are diagrammatically represented in Fig. 1, for the concentration of sulphuric acid, and in Fig. 2 for the sodium hydroxyde.

In the case of sodium hydroxyde, the potentials vary almost in linear manner with the logarithm of the concentration, as may be seen in Fig. 2; whereas in the case of sulphuric acid the same relation holds only under the concentration of 10^{-2} normal, as may be seen in Fig. 1.

1) FALES and MUDGE, loc. cit.





In order to examine whether or not the potential of pyrite is quite independent of the sodium or sulphate ion concentration, the measurements were carried out employing the solution of Na₂SO₁ of various concentrations. Results are cited in Table III.

Regardless of the change in concentration, the results are practically constant, the total mean being 0.665 volts.

When the pyrite is immersed in the sulphuric acid, the hydrogen sulphide, in all possibility, would be produced on its surface, even though it may merely be a trace, as the result of some chemical action of pyrite itself. If so, the potential of pyrite should assume rather a lower value than otherwise especially in highly concentrated acid. Probably, this is the reason why the potentials against 6n-H₂SO₄ are always lower than those against the n-H₂SO₄.





Electrodes	I (volt)	II (volt)	III (volt)	IV (volt)
Sat. Na₂SO₄	0.665	0.651	0.665	0.668
n "	0.671	0.659	0.670	0.672
10-1 ,,	0.666	0.662	0.666	0.672
10-° "	0.665	0.652	0.663	0.672
10-3 "	0.671	0.657	0.652	0.672
10-4 "	0.670	0.657	0.659	0.667
Mean	0.668	0.656	0.663	0.671
Total me	an			0.665

Table III

Electrode: (100) of pyrite from Tsunatori.

III. Effects of Hydrogen Ion Concentration upon the Potential of Pyrite

After the previous experiments, it is evident that the potential of pyrite against the acid or alkaline solution is remarkably responsible for the hydrogen ion concentration of the solution. The magnitude of the latter in solutions which were used in the previous experiments may be taken approximately as follows.

Т	à	bl	le	Ι	V
-	~	~	~		

Solutions	Hydrogen ion conc.	pH	Remarks (Various calculated values of hydrogen ion conc.
n-H ₂ SO ₄	0.52	0.28	0.53363) 0.5175)
10-1 "	0.059	1.23	$\begin{array}{cccc} 0.0585^{1)} & 0.0625^{2)} & 0.0555^{3)} \\ 0.05859^{4)} & 0.0587^{6)} \end{array}$
10-2 ,,	0.0082	2.09	0.00825 ¹) 0.0081 ²) 0.00804 ⁵)
10-3 "	0.00094	3.03	0.000943 ⁵)
10-1 ,,	0.0001	4.00%)	
10 ⁻⁵ "	0.00001	5.00°)	

a) Sulphuric acid

1) Noves and Stewart, J. Amer. Chem., 32, 1133 (1910).

2) These values were obtained from conductance data by Noves and Stewart.

Table IV (Continued)

Sodium hydroxyde. The pH-values were calculated b) from the hydroxyde ion concentrations assuming the dissociation constant of the water as 0.72×10^{-14} at $18^{\circ}C^{.7}$

Solutions	Hydroxyde ion conc.	pH	Remarks (Various calculated values of) hydroxyde ion conc.
n-NaOH	0.72	14.00	0.722 ^s) 0.725 ¹¹)
10-1 "	0.090	13.10	0.0899 ^s) 0.0903 ¹¹)
10-2 "	0.0094	12.12	$\begin{array}{c} 0.00935^{11}) & 0.00936^{9} \\ 0.00939^{11} \end{array} \\ \begin{array}{c} 0.00936^{11} \end{array} \\ \end{array} \\ \begin{array}{c} 0.00936^{11} \end{array} \\ \end{array}$
10-3 .,,	0.0011:)	11.14	
10-4 "	0.000111)	10.14	
10-5. "	0.0000112)	9.14	

3) T. ONODA, ZS. anorg. Chem., 165, 137 (1927).

These values were calculated from the results of the equivalent conductivity and the specific viscosity at 30°C according to the following equation:

$$C_{H} = Cn\left(\frac{\Lambda}{\Lambda_{\infty}} \cdot \frac{\eta}{\eta}\right)$$

where C_{H} stands for the hydrogen ion concentration, C_n , the normality of sulphuric acid, A and Λ_{∞} the equivalent conductivity at the given and the maximum dilution, η and η_{∞} , the viscosity of the given solution and the water respectively.

4) J. E. ENKLAAR, ZS. phy. Chem., 80, 617 (1912).
5) The writer had calculated only from the following data of the equivalent conductivity. According to KOHLRAUSCH [Landolt-Börnstein phy.-chem. Tabellen, II, 5 Aufl. Berlin, S. 1081 (1923)],

 $\Lambda = 198$ (Normal)

=225(0.1 Normal) at 18°C.

=308 (0.01 Normal) $=361 \quad (0.001 \text{ Normal})$

According to Noves and co-workers [ZS. phy. Chem., 70, 362 (1910)]

at 18°C. $\Lambda_{\infty} = 383$

6) Sulphuric acid was assumed to be in a completely dissociated state.

7) R. LORENZ and BÖHI, ZS. phy. Chem., 66, 748 (1909).

8) ABEGG'S Handbuch der anorganischen Chemie, II, Abteil. 1, S. 246 (1908).

9) This value was obtained from the dissociation degree which was interpolated between the two, 94. 1 and 93.0% at 0.009458 and 0.01058 normal reported by H. C. JONES [ZS. phy. Chem., 12, 639 (1893)].

10) A. A. NOYES, A. C. MELCHER, H. C. COOPER and G. W. EASTMAN, ZS. phy. Chem. 70, 362 (1910).

11) The present writer had calculated only from the data of the equivalent conductivity. According to KOHLRAUSCH [Landolt-Börnstein phy.-chem. Tabellen, II, 5 Aufl. Berlin, S. 1082 (1923)],

 $\Lambda = 157$ (Normal) =195.4 (0.1 Normal) at 18°C.

=203.4 (0.01 Normal)

According to Noves and co-workers

 $\Lambda_{\infty} = 216.5$ at 18°C.



The relation between the potential and pH-value of the solution is diagramatically represented in Fig. 3. There we adopted 0.665 volts, which was obtained as the mean value of pyrite potential against the solution of Na_2SO_4 in the foregoing experiment, as that against a neutral solution whose pH-value can be calculated as 7.07 from the dissociation constant of water.

As may be distinctly seen in Fig. 3, the potential variation is nearly accordant with that of pH of the solution in the linear manner.

To demonstrate the above statement

with more certainty, the following experiment was undertaken. 100 c.c. of n/10-H₂SO₄ was taken as the initial solution and the air was completely expelled from it as illustrated before. The pyrite electrode was then immersed in this solution and electrically connected to a calomel electrode. The electromotive force of the combined cell was measured when it had settled nearly to a constant. A suitable amount of n/10-NaOH was added to the initial solution from time to time and the measurements were repeated at each step of addition. The potential of pyrite electrode was calculated from the electromotive force of the cell and the potential of calomel electrode.

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¹²⁾ Sodium hydroxyde was assumed to be in the state of complete dissociation. According to H. C. JONES, the dissociation degree of the solution of 0.001058 normal is 100%.

Table V

I	II	III	IV
$\begin{array}{c} 0.911\\ 0.898\\ 0.872\\ 0.837\\ 0.823\\ 0.802\\ 0.781\\ 0.661\\ 0.503\\ 0.465\\ 0.437\\ 0.427\\ 0.411 \end{array}$	$\begin{array}{c} 0.949\\ 0.934\\ 0.915\\ 0.856\\ 0.856\\ 0.843\\ 0.826\\ 0.669\\ 0.534\\ 0.492\\ 0.454\\ 0.438\\ 0.417\\ 0.438\\ 0.417\end{array}$	$\begin{array}{c} 0.895\\ 0.875\\ 0.851\\ 0.793\\ 0.793\\ 0.791\\ 0.773\\ 0.657\\ 0.520\\ 0.486\\ 0.455\\ 0.440\\ 0.419\\ 0.$	$\begin{array}{c} 0.895\\ 0.876\\ 0.876\\ 0.808\\ 0.808\\ 0.808\\ 0.804\\ 0.782\\ 0.652\\ 0.540\\ 0.540\\ 0.507\\ 0.466\\ 0.448\\ 0.427\\ 0.427\end{array}$
	I 0.911 0.898 0.872 0.837 0.823 0.802 0.781 0.661 0.503 0.465 0.437 0.427 0.411 0.392	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Initial solution : 100 c.c. of n/10-H₂SO₄ Electrode : (100) of pyrite from Tsunatori.

are summarized in the above table, and the relation between the potential and the volume of n/10-NaOH is graphically represented in Fig. 4.

Under the same operation, J. E. ENKLAAR¹⁾ had already determined the pHvalue at each step of the addition of n/10-NaOH. The so called titration curve he thus obtained is shown in Fig. 4 drawn through the points marked by crosses to distinguish it from the writer's curves. As one might expect, the dispositions of the writer's curves are quite similar with the titration curve of ENKLAAR, i.e. the variations of the pyrite potential and pH of the solution

1) J. E. ENKLAAR, loc. cit.

Fig. 4



Table VI

n/10-NaOH	-11	Potential of pyrite electrode (volt)				
added (c.c.)	рп	I	II	III	IV	
0	1.2322	0.914	0.950	0.890	0.895	
20	1.3414	0.902	0.938	0.885	0.887	
40	1.5182	0.889	0.927	0.868	0.870	
60	1.7261	0.873	0.914	0.852	0.856	
80	2.0589	0.852	0.897	0.830	0.837	
90	2.3969	0.834	0.879	0.817	0.825	
95	2.7262	0.817	0.858	0.797	0.817	
100	7.1543	0.661	0.667	0.657	0.652	
105	11.669	0.438	0.454	0.455	0.463	
110	12.085	0.408	0.415	0.419	0.425	



similarly show a rapid change at the neutral point. Therefore it is safe to assume that the variation of the pyrite potential is based upon the hydrogen ion concentration of the solution.

On each curve in Fig. 4, the pyrite potential at each step of the addition of n-NaOH is interpolated and the values thus obtained were correlated to the corresponding pH-values which were actually obtained by ENKLAAR. The results are shown in Table VI.

According to the above data, the relation between the potential and pH-value could be expressed by almost linear curves as is shown in Fig. 5.

IV. Pyrite Potential against Sulphide Solution

In order to determine the effects of change in the concentration of sulphide solution upon the potential of pyrite, the following ex-

Electrodes Solutions	I (volt)	II (volt)	III (volt)	IV (volt)	Mean	
n-Na ₂ S	-0.190	-0.216	-0.213	-0.189	-0.202	
10-1 ,,	-0.006	-0.042	-0.033	-0.006	-0.022	
10-2 ,,	0.149	0.125	0.137	0.157	0.142	
10-3 ,,	0.306	0.296	0.279	0.294	0.294	
10-4 "	0.455	0.439	0.406	0.440	0.435	
10-5 "	0.505	0.546	0.460	0.514	0.506	

Table VII Electrode: (100) of pyrite from Tsunatori

periment was undertaken. Sodium sulphide solutions of various content ranging from normal to 10^{-5} normal by tenfold dilution were prepared. The pyrite potentials against these solutions were respectively determined in the order of concentration under the same procedure as before. Results are shown in the above table.

The relations between the potential and the logarithm of concentration are given in Fig. 6.

The pyrite potential against n-Na₂S is considerably lower than that against n-NaOH, their difference being ca. 0.5 volts. This fact may be ascribed to the presence of hydrosulphide



or sulphide ion as their hydrogen ion concentrations are considered to be neary the same.

Whereas the hydrosulphide or sulphide ion concentrations are decreased with the dilution, the hydrogen ion, on the contrary, is increased: but those variations are by no means restricted by the relation of solubility product of hydrogen sulphide. In this circumstance, the potential variations are far greater than those in the case of the solution of sodium hydroxyde for the same interval of change of the concentration.

To determine the effect of hydrogen ion concentration on the pyrite potential, the following experiments were undertaken. 100 c.c. of $1.028 \text{ n-H}_2\text{SO}_1$ was syphoned into a glass jar with a capacity of about 200 c.c. The pyrite electrode was immersed in the solution by means of the gum stopper in which the electrode was inserted. After perfect saturation of the solution with hydrogen sulphide, a

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Initial solution : 100 c.c. of 1.028 n-H₂SO₄ Electrode : (100) of porite from Tsunatori.

n-Na ₃ S added	Potential of pyrite electrode (volt)					
(c.c.)	I	II	III	IV		
0	0.976	0.950	0.991	0.976		
Satd. w. H ₂ S	0.522	0.530	0.564	0.502		
20	0.470	0.465	0.503	0.451		
40	0.435	0.433	0.470	0.424		
48	0.416	0.423	0.455	0.411		
49	0.413	0.421	0.441	0.410		
50	0.408	0.416	0.440	0.405		
52	0.412	0.415	0.440	0.405		
60	0.399	0.405	0.425	0.396		
80	0.377	0.372	0.399	0.369		
90	0.354	0.349	0.371	0.348		
93	0.345	0.344	0.353	0.339		
96	0.328	0.327	0.343	0.330		
99	0.312	0.308	0.325	0.314		
100	0.302	0.300	0.319	0.306		
101	0.296	0.290	0.313	0.301		
102	0.284	0.277	0.298	0.291		
103	0.160	0.153	0.174	0.164		
110	0.044	0.040	0.056	0.051		
120	0.017	0.011	0.025	0.018		
130	-0.012	-0.012	-0.007	-0.012		



suitable quantity of n-Na₂S was added to the solution. The pyrite potentials at each step of the addition were determined just as before. In this case, the variation of hydrogen and hydrosulphide or sulphide ion concentrations are always subjected to the relation of the solubility product of hydrogen sulphide.

By introducing hydrogen sulphide into the initial solution of $1.028 \text{ n-H}_2\text{SO}_4$, the pyrite potential underwent a considerable change, but after perfect saturation it showed ca. 0.53 volts.

The results are

tabulated in Table VIII, and the relation between the potential and the volume of n-Na₂S is diagrammatically represented in Fig. 7.

The curves which again resemble the titration curve, show us well that the potential behaviors depend on the hydrogen ion concentration. To represent this relation more certainly, the relation between the potential of pyrite and pH of the solution is diagrammatically shown in Fig. 8 employing the figures in Table IX. That the potential stands in a linear relation with pH is quite clear.

Solutions	Hydrogen ion conc.	pH	Potential	of pyrite	e electrode (volt)
$n-H_2SO_4$ satd. w. H_2S	0.53	0.28	0.522 0.502	0.530 0.588	0.564) Mean 0.548) 0.542
n/10-Na ₂ SO ₄ satd. w. H ₂ S	0.9×10-4 1)	4.05	0.303 0.302	0.313	0.303}Mean } 0.305

Ta	ble	IX

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Solutions	Hydrogen ion conc.	pH	Potential of pyrite electrode (volt)
Neutral soln. satd. w. H ₂ S	0.85×10-7 2)	7.07	0.16 ³⁾
n-NaSH	3.3×10 ^{-11 4})	10.48	-0.035)
2n-Na ₂ S	1.3×10 ⁻¹⁴ ⁶)	13.89	-0.237 -0.230 -0.216}Mean -0.196 }-0.220

Table IX (Continued)

V. Experimental Formulas for the Potential of Pyrite Electrode



According to the previous experimental results, the potential of pyrite could be regarded as the linear function of pH of the solution as shown in Fig. 9. Therefore we may write the general expression of the pyrite potential as follows:

$E = E_0 - k.pH$

where E_0 and k show the constants which are quite independent of the concentration but depend on the nature of solution. Here the constant E_0 , which corresponds to the potential against a solution whose pH is zero, could be obtained by the graphical extrapolation with the help of the nearly linear function as 1.007 volts in the case of the acid and alkaline solution. Hence the equation becomes

E = 1.007 - k.pH.

By substituting E and pH in the

1) According to FALES [Inorganic Quantitative Analysis, p. 159 (1928)], the hyrogen ion concentration of hydrogen sulphide water is 0.9×10^{-4} .

2) This value was calculated from the dissociation constant of water.

3) From the curves given in Fig. 7, this value was approximately obtained as the potential corresponding to that at neutral state.

6) FALES, loc. cit.

⁴⁾ FALES, loc. cit.

⁵⁾ R. C. Wells, loc. cit.

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Ta	ble	Х

Solutions	pH	E	k
n-H ₂ SO ₄ 10 ⁻¹ ,, 10 ⁻² ,,	0.28 1.23 2.09	0.946 0.936 0.905	0.058 (?) 0.049
10^{-3} ,,	3.03	0.853	0.051
10^{-4} ,,	4	0.802	0.051
10^{-5} ,,	5	0.750	0.051
n/10-Na ₂ SO ₄	7.07	0.665	0.048
10 ⁻⁵ n-NaOH	9.14	0.587	0.046
10 ⁻⁴ "	10.14	0.519	0.048
10^{-3} ,,	$ 11.14 \\ 12.12 \\ 13.10 \\ 0 $	0.465	0.049
10^{-2} ,,		0.416	0.049
10^{-1} ,,		0.371	0.049
n "	14.00 	0.320	0.050



above equation with the corresponding experimental results, we get the constant k according to the following equation:

$$k = \frac{1.007 - E}{\text{pH}}$$

For the calculation of k, we adopted the mean values of pyrite potentials given in Tables I, II and III as E. The results are summarized in Table X.

There is a fair approach to constancy in the value of k, its mean value being 0.050. This is quite sufficient to show that the potential of pyrite electrode in this case may be expressed by the following experimental formula:

> E=1.007-0.050. pH, E=1.007+0.050. Log [H⁻].

or

In the case of the sulphide solution, the potential variation and pH change of the solution is in the linear manner but with opposite sense just as in the case of the acid and alkaline solution. Therefore the following equation should also be applicable for the potential behaviors in this case:

$$E = E_{v} - k.pH.$$

The value of E_0 is easily obtained by means of the graphical extrapolation as 0.557 volts. By substituting E and pH with the results shown in Table IX we get k at various values of pH. The results thus obtained are as follows.

Solutions	$_{\rm pH}$	E (volt)	k
n-H ₂ SO ₄ satd. w. H ₂ S	0.28	0.542	0.054
n/10-Na ₂ SO ₄ satd. w. H ₂ S	4.05	0.305	0.062
Neutral solution satd. w. H ₂ S	7.07	0.16	0.056
n-NaHS	10.48	-0.03	0.056
2n-Na₂S	13.89	-0.220	0.056

Table XI

As there is fair approach to constancy in the value of k, whose mean value is precisely identical with $\frac{RT}{F} = 0.055$ at 18°C, so we may write the general experimental formula for the pyrite potential as:

or

E = 0.557 - 0.056. pH E = 0.557 + 0.057. Log [H^{*}]

VI. Conclusion

1) The potential of a pyrite electrode depends to a remarkable degree on the hydrogen ion concentration of the solution. But it is quite independent of the sodium or sulphate ion concentration.

2) In the case of acid or alkaline solution, the pyrite potential corresponding to that against the solution whose pH-value is zero is 1.007 volts; whereas in the case of sulphide solution, it is only 0.557 volts.

3) The following two experimental formulas are proposed for the calculation of potential of pyrite electrode;

- a) E = 1.007 + 0.050 Log [H']
- b) E = 0.557 + 0.057 Log [H]

a) is applicable for the acid or alkaline solution; and b) for the sulphide solution.

In conclusion, the writer wishes to express his sincere thanks to Prof. A. MATSUBARA for his kind guidance during this research.