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Studies on the Surface Characters of Minerals (1) : Electro-chemical Behavior of the Crystal Surface of Pyrite

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CITATION:

Matsubara, Atsushi. Studies on the Surface Characters of Minerals (1) : Electro-chemical Behavior of the Crystal Surface of Pyrite. Memoirs of the College of Science, Kyoto Imperial University. Ser. B 1924, 1(4): 285-332

ISSUE DATE:

1924-12-25

URL:

<http://hdl.handle.net/2433/257675>

RIGHT:

Studies on the Surface Characters of Minerals.

1. Electro-chemical Behavior of the Crystal Surface of Pyrite.

By

ATSUSHI MATSUBARA.

With Plate XIX and 5 Text-figures.

Introductory.

The potential difference between a crystal surface and a given solution is supposed to be a function of the atomic arrangement of the surface, and since the latter differs in different crystal faces, the potential ought to be different according to the kind of crystal face.

This simple inference has induced the author to take up the experimental examination of the fact. The conclusion arrived at from the author's investigation was affirmative, and may be summarised as follows:

- 1) A definite crystallographical surface assume a definite potential against a given solution, but different surfaces show different potentials.
- 2) The actual atomic surface which determines the value of the potential often differs from the macroscopical or microscopical crystal face which is the surfacc of the electrode. This comes from the existence of extremely fine engravings on an apparently smooth crystal face.
- 3) The variation of the potential of a pyrite electrode with time is to be ascribed to the decomposition of the pre-existing atomic surface, and the subsequent formation of new ones.

The surfaces of the more simple crystallographical indices are more stable and persist for a longer time.

- 4) If the number of "free crystalline bonds" exposed in a unit area of the surface be called as "the surface density of free crystalline bond," the potentials shown by different atomic surfaces against a given solution are proportional to their surface densities of free crystalline bond.
- 5) The electrical phenomena exhibited by a pyrite electrode are chiefly due to the action of its sulphur atoms. The ion which carries the electricity is SH^- ion.

Although the research is only at its beginning, and experiments with some other minerals than pyrite are not yet completed, the author has thought it better to call general attention to what he has already done.

General Method of Investigation.

The electro-chemistry of the pyrite electrode was first extensively studied by R. C. Wells¹⁾ who gave us much important information about the nature of several mineral electrodes. He came to the conclusion that the potential of a pyrite electrode is presumably due either to the "ferric-ferrous" potential or to the "sulphidé" potential.

G. Tammann²⁾ studied the phenomena of the interchange of cations between the atomic skin of mineral surfaces and various solutions. He found that a pyrite behaves more positively than the hydrogen electrode in the solution, which fact he ascribed to the passive state of the iron on the surface of the mineral. Unfortunately, however, he did not touch the function of sulphur atoms on the surface, a matter which was beyond the scope of his investigation.

Thus, the fundamental chemical mechanism of the electrical phenomena in the pyrite electrode remains still unsettled. In spite of

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

2) G. Tammann, Über die Ionenaustausch an der Oberfläche von Mineralien. Zeitschr. f. anorg. Chem. 113, 149 (1920).

this difficulty, the natural crystals of pyrite are usually rich in smooth faces of several different indices, and the atomic arrangement in the crystal is fully determined by W. H. and W. L. Bragg.¹⁾ For this reason the author has preferred, first of all, to take pyrite as the material for the experiment.

To make use of a crystal face of pyrite as an electrode, special care was taken to select a face which was perfectly smooth and shining being free from all sorts of mechanical and chemical scars, striations, vicinal faces or gildings. A few preliminary experiments showed that it must be at least larger than one square milimeter, for otherwise its potential can not be determined with any great accuracy. Crystal faces satisfying these requirements are very rare indeed, and we can pick up only a few from dozens of specimens.

Fortunately, Prof. T. Hiki was so generous as to offer the author, to his great joy and gratitude, all of his precious collection of pyrite consisting of more than six hundred separate crystals from Sagi. All the specimens from that locality which were used in this research and are now in use originate from this collection.

Attention was first paid to the potentials of various crystal faces chiefly belonging to the zone (100)/(110). The measurement was accomplished as follows:

A shallow paraffin vessel, with a capacity of about 20 ccm., was separated into two parts by a septum also made of paraffin. The septum had a suitable hole through which a crystal of pyrite was thrust so that the crystal face under examination only was exposed on the one side of the septum. If any other faces, edges etc. were exposed on that side of the septum, they were thoroughly covered by melted paraffin, and even the margin of the face under examination was not allowed to be exposed. Where the face had any imperfection, that part of the face was also covered with paraffin.

The face under examination was previously cleaned by gently

1) W. H. Bragg and W. L. Bragg, X-rays and Crystal Structure, P. 130 (1920).

wiping with cotton wool, which had been moistened with ether, in order to remove any grease, dust, rust, etc. All trace of ether was thoroughly vapourised in the air before fastening it to the paraffin septum.

To that side of the septum where the crystal face was exposed, the solution was made to run down continually through a glass tube and to wash the surface of the electrode in order to prevent the polarization of the latter.

The connection between the pyrite electrode and a potentiometer was first made by a copper wire one end of which was fastened directly to the crystal. But soon afterwards, this procedure of connection was given up; a mercury connection between the crystal and a piece of platinum wire on the one side, and another mercury connection between the platinum and the potentiometer on the other were used instead. It was because the two kinds of connection made no measurable difference in the value of the potential at the room temperature, and the latter method was more convenient.

The side tube of a normal calomel electrode was dipped into the solution in the paraffin cell. The superfluous solution in the cell was made to run down through a drainage channel the amount of flow being regulated to be ca. 200 ccm. in one hour.

A potentiometer of the Leeds and Northrup Type K with a galvanometer of fairly high sensibility was employed. Attention was paid to maintain the room temperature as constant as possible at 18°C.; no greater deviation than $\pm 2^\circ$ was ever observed.

Experiment with Normal Potassium Chloride.

By a few preliminary experiments, it was found that the potential varies greatly with time so that it is rather difficult to determine which is the proper potential for the electrode under examination. So the author thought it necessary first to examine the manner of variation of

the potential with regard to time, and to find the final value if the electrode "settles."

In making the circuit of the combined cell, the pyrite always formed the positive electrode. Hence, its potential is to be obtained by adding the potential of the calomal electrode, namely 0.560 volt, to the observed potentials of the cell. In the following tables, the observed potentials of the cell only are mentioned.

Table 1.

Exp. No. 1.

Electrode: (210) of pyrite from Udo.

Time in minutes.	Reading of potential.	Time in minutes.	Reading of potential.
2.7	0.2031	25	0.1766
5	0.1995	32	"
11	0.1742	42	"
15	0.1766	50	"
18	"	66	"
20	"		

Table 2.

Exp. No. 2.

Electrode: (100) of pyrite from Udo.

Time in minutes.	Reading of potential.	Time in minutes.	Reading of potential.
1	0.2051	41	0.2014
2.5	0.2005	42.5	0.2010
5	0.2008	45	0.2028
8	"	46	0.2032
15	0.2011	47	0.2037
16	0.2005	49	0.2045
22	0.2015	50	0.2052
23	0.2017	52	0.2022
24	0.2012	54	0.2010
25	"	55	0.2000
27	0.2020		
28	0.2012	Left standing overnight.	
29	0.2005	1262	0.2301
30	"	1267	0.2292
31	"	1268	0.2281
33	"	1269	"
35	0.2000	1272	"
38	0.2008	1275	"
39	"		
40	"		

Exp. No. 3.

Table 3.

Electrode : (100) of pyrite from Udo.

Time in minutes.	Reading of potential.	Time in minutes.	Reading of potential.
3	0.1572	27.5	0.1670
5	0.1498	29	0.1687
7	0.1441	32	0.1710
10	0.1436	36	0.1709
12	0.1445	43	0.1710
14	0.1482	45	0.1708
16.5	0.1525	50	0.1672
18	0.1561	58	0.1700
20	0.1602	62	0.1707
22	0.1632	64	0.1708
24	0.1652	67	0.1716

Exp. No. 4.

Table 4.

Electrode : (100) of pyrite from Udo.

Time in minutes.	Reading of potential.	Time in minutes.	Reading of potential.
2	0.1877	104	0.1714
4	0.1238	107	0.1711
6	0.1331	111	0.1737
7.5	0.1424	114	0.1756
12	0.1777	116.5	0.1770
15	0.1710	121	0.1788
17.5	0.1655	125	0.1790
18	0.1604	130	„
30	„	140	0.1815
42	0.1499	145	„
57	0.1561	150	0.1829
66	0.1615	165	0.1832
71	0.1648	170	0.1835
75	0.1667	174	„
80	0.1692	177	0.1824
85	0.1705	180	„
89	0.1703	185	„
95	0.1707	190	„
97	0.1718	200	0.1835
100	0.1725	204	0.1840

Table. 4.

Continued.

Time in minutes.	Reading of potential.	Time in minutes.	Reading of potential.
205	0.1843	1350	0.1847
210	"	1355	0.1850
226	0.1873	1390	0.1875
232	"	1410	0.1900
240	"	1412	0.19081
253	"	1418	"
270	0.1888	1422	"
287	0.1895	1432	"
297	0.1904	1450	0.1911
327	0.1919	1479	0.1914
Left standing over night.			
1300	0.1892		
1305	0.1852		
1307	0.1843		
1310	"		
1315	"		
1324	"		
1328	"		

Table. 5.

Exp. No. 5.

Electrode : (211) of pyrite from Udo.

Time in minutes.	Reading of potential.	Time in minutes.	Reading of potential.
2	0.17790	10	0.20599
4	0.20430	11	0.20530
6	0.20350	16	0.20320
7	0.20045	28	0.20620
8	0.20179		
9	0.20297		

Table. 6.

Exp. No. 6.

Electrode : (111) of pyrite from Udo.

Time in minutes.	Reading of potential.	Time in minutes.	Reading of potential.
2	0.10000	17	0.09805
3.5	0.08200	19	0.10094
5	0.07805	20	0.10552
9	0.07988	22	0.11092
10	0.08010	23	0.11170
12.5	0.08883	33	0.12430
14	0.09180	43	0.13041

Table 6.

Continued.

Time in minutes.	Reading of potential.	Time in minutes.	Reading of potential.
85	0.14277	255	0.16106
170	0.14905	276	0.17055
173	0.15610	407	0.17120
175	0.16070		
222	"		

Table 7.

Exp. No. 7.

Electrode : (111) of pyrite from Sagi.

Time in minutes.	Reading of potential.	Time in minutes.	Reading of potential.
1.5	0.21326	15.5	0.20340
2.5	0.21040	16	0.20176
3.6	0.20675	22.5	0.19124
5	0.21132	24	0.19030
6	0.21575	25	0.19305
7.5	0.21530	27	0.19246
10	0.21483	29	0.19846
11.5	0.21218	31	0.19748
12.3	0.20995	34	0.19527
13	0.20794	42	"
14	0.20630	50	0.19832

So far as the above experiments are concerned, it appears impossible to say that a definite crystal face should show a definite potential. In exp. No. 1, (210) gave a voltage of 0.20 at the beginning, but the same voltage was obtained in (100) at the beginning of exp. No. 2, also in (211) and (111) in the course of the variation of voltage as can be seen in exps. No. 5 and 7. The value 0.17 volt seems to be the settled potential for (210) as is seen in exp. No. 1, but the same appears to be also true with (100) as is seen in Exp. No. 3. Exp. No. 2 shows that 0.20 or else 0.22 volt may be suspected to be the proper potential for (100), but No. 3 and 4 prove quite otherwise.

That the potential was not essentially affected by polarisation is proved by the gradual rise of the former in many experiments.

One thing which is peculiar to the phenomena is the predominance of certain definite voltages in several experiments regardless of the

kind of crystal face. Taking the rough number, the voltages of 0.20, 0.191, 0.177 and 0.171 seem to appear in several different experiments and last for longer periods than the other values of voltage. In order to examine the matter more closely, eight more experiments were carried out chiefly using (100) of pyrite from Udo as the electrode. The result was affirmative; the above generalization was thoroughly proved. Moreover, it was found that one and the same electrode can give several of the predominant voltages which are common in other electrodes so that the variation is apt to occur in step-wise. This fact will be re-considered in later chapters.

R. C. Wells¹⁾ has also obtained a number of different values of the potential with pyrite electrodes against normal KCl solution, though the conditions of experiment were somewhat different from those of the present author. According to Wells, the potential shown by a pyrite electrode in the open air must presumably be ascribed either to the ferric-ferrous potential resulting from the inevitable production of ferric salt by the action of air, or to the "sulphide" potential which is produced from the reducing action of the sulphide ions, for instance, upon ferric ions.

If Wells's opinion holds true, the characteristic potential of each crystal face should be found by measurements in the "absence of air," or more precisely, in a solution which contains no "excess of oxygen or hydrogen over the amounts necessary to form water".

According to Wells's calculation, all neutral solutions imparting a potential of 0.676 volt to an unattackable electrode contain no excess of free hydrogen or free oxygen. Keeping this in mind, the present author has tried to find the proper potentials for crystal faces in neutral KCl solution when the latter imparts a potential of 0.676 volt to a platinum electrode.

Measurements were made in a confined space from which air could be completely expelled by a current of hydrogen or nitrogen. For the

1) R. C. Wells, loc. cit. p. 32.

purpose of introducing oxygen, a current of air could likewise be led into the space. The apparatus used is diagrammatically represented in Fig. 1.

A is a large glass tube whose lower end was closed by a pyrite crystal M. The latter was fastened to the tube by paraffin which covered the whole crystal body except the part of the crystal face under examination. The connection of the crystal to the potentiometer

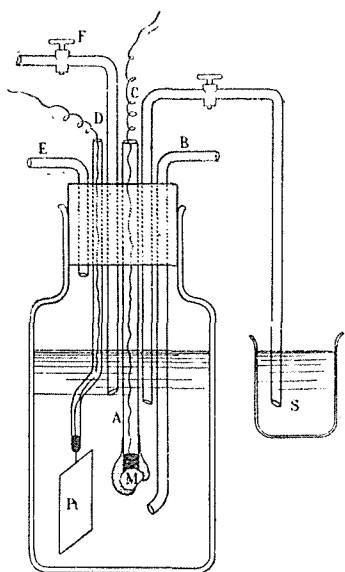


Fig. 1.

was made by mercury and platinum wire as was illustrated before. B is the conducting tube for gasses which were previously passed through a tower containing normal KCl solution in order to avoid any loss of water in the half cell by evaporation.

Pt is the blank platinum electrode having an area of ca. 4 sq. cm. This was previously ignited and so placed in the half cell that it sank entirely beneath the surface of the solution.

The experimental results are given in Tables 8 to 11. In combination with a normal calomel

electrode, pyrite always formed the positive pole, while the platinum formed sometimes the positive and sometimes the negative pole. In the former case, the voltage of the cell is represented by +, and in the latter by the - sign.

Table 8.

Exp. No. 16.

Electrode: (100) of pyrite from Udo.

Time in Minutes.	Voltage of the Cell:	
	Hg/HgCl/KCl/pyrite.	Hg/HgCl/KCl/Pt.
3	0.2033	
5	0.20576	
6	0.20485	
7	0.21157	
10	0.21686	
14	0.22165	
24	0.24035	
Hydrogen was bubbled in the cell and was made to rub the surface of the pyrite continually.		
32	0.20195	
45		-0.17306
50	0.26400	
57		-0.41941
60	0.2688	
83	0.28150	
113	0.28150	
281	0.28340	
295	0.28285	
404	0.28245	-0.53215
465	0.27723	-0.54400
500	0.27436	-0.54435
513	0.27350	-0.54555
528	0.27265	-0.54509
Left standing overnight, the current of H ₂ being stopped.		
1615	0.27727	-0.13872
Air was bubbled in.		
1640	0.27984	-0.08637
1660	0.27974	-0.06512
1680	"	-0.05785
1692	0.27922	-0.04795
1704	"	-0.03380
1716	"	-0.01520
1728	"	0.00200
1740	0.27905	0.02720
1752	0.27775	0.04075
1764	"	0.04780
1779	0.27751	0.05109
1788	"	0.05675
1830	0.27784	0.06225
Left standing overnight, the current of air being stopped.		
2790	0.27775	0.07584
Air was bubbled in.		
2800	0.27488	0.10664
		"Pure water" potential.
2815	0.27409	0.14615
2825	0.27318	0.15725
2830	"	0.16237
2840	0.27235	0.16345
2855	0.27250	0.17115
2860	0.27180	0.17290

Table 8.

Continued.

Time in Minutes.	Voltage of the Cell :	
	Hg/HgCl/KCl/pyrite.	Hg/HgCl/KCl/Pt.
Air was stopped, H ₂ was bubbled in.		
2870	0.27185	0.14965
2883	0.27220	-0.11265
2895	0.27085	-0.16515
2913	0.27090	-0.19085
2930	"	-0.20485
2947	0.27105	-0.21080
2990	0.27090	-0.23114
3010	0.27070	-0.24260
3055	0.27055	-0.26027

Table 9.

Exp. No. 17.

Electrode : (210) of pyrite from Udo.

Time in Minutes.	Voltage of the Cell :	
	Hg/HgCl/KCl/pyrite.	Hg/HgCl/KCl/Pt.
5	0.17350	-0.05230
Air was bubbled in.		
25	0.16560	-0.06913
32	0.16740	-0.04020
37	0.16700	-0.03311
39	0.17125	
42	0.17295	
43		-0.01410
51	0.17130	-0.00665
70	0.17215	0.04496
75	0.17365	0.04096
77	0.17770	0.10021
84	"	0.10613
89	"	0.11130
— " Pure water " potential.		
94	0.17506	0.12142
100	0.17435	0.12737
110	0.17423	0.13676
115	"	0.14005
120	0.17230	0.14692
H ₂ was bubbled in.		
240	0.1782	0.0278
248	0.1780	-0.0773
256	0.1790	-0.0909
264	0.1778	-0.1184
272	0.1755	-0.1540
Air was bubbled in.		
280	0.1730	-0.1510
288	"	-0.1360
296	0.1721	-0.1273

Table 9.

Continued.

Time in Minutes.	Voltage of the Cell :	
	Hg/HgCl/KCl/pyrite.	Hg/HgCl/KCl/Pt.
304	0.17355	-0.0845
312	0.1722	-0.0510
320	0.1753	-0.0358
328	0.1770	-0.0165
336	"	0.0050
344	"	0.0302
352	0.1778	0.0494
360	0.1796	0.0854
Left standing overnight, air being stopped.		
1020	0.1829	0.1656
H ₂ was bubbled in.		
1025	0.2030	
1030	0.2080	0.1000
1050	0.2112	
1065	0.2149	-0.0380
Air was bubbled in.		
1075	"	0.0042
1090	0.2194	0.0309
1105	"	0.0468
1120	"	0.0581
1135	"	0.0753
1150	0.2183	0.0928
1175	0.2170	0.1041
1190	0.2231	0.1525
—	—	" Pure water " potential.
1200	0.2208	0.1727
Air was stopped; H ₂ was bubbled in.		
1220	"	0.1350
—	—	" Pure water " potential.
1240	"	0.1023
1260	"	0.0048

Table 10.

Exp. No. 18.

Electrode : (100) of pyrite from Udo.

Time in Minutes.	Voltage of the Cell :	
	Hg/HgCl/KCl/pyrite.	Hg/HgCl/KCl/Pt.
5	0.3044	-0.0167
8	0.3034	
Air was bubbled in.		
10	0.2979	-0.0094
13	0.2912	
14	0.2901	

Table 10.

Continued.

Time in Minutes.	Voltage of the Cell :	
	Hg/HgCl/KCl/pyrite.	Hg/HgCl/KCl/Pt.
15	0.2885	0.0052
18	0.2884	0.0148
20	0.2863	
24	0.2822	0.0382
32	0.2758	0.0630
34	"	0.0770
41	"	
44	0.2755	0.1029
45		0.1050
Nitrogen was bubbled in.		
55	0.2771	" Pure water " potential.
62	0.2839	0.1258
65		0.1294
74	0.2813	0.1306
76	0.2807	"
77	0.2800	"
80	0.2793	0.1382

Table 11.

Exp. No. 19.

Electrode : (210) of pyrite from Sagi.

Time in Minutes.	Voltage of the Cell :	
	Hg/HgCl/KCl/pyrite.	Hg/HgCl/KCl/Pt.
18	0.3410	
23	0.3398	
Air was bubbled in.		
30	0.3362	0.0680
33	"	
35	0.3353	0.0810
38	"	
53	0.3328	" Pure water " potential.
60	0.3316	
68	"	
73	0.3300	0.1375
159	0.3283	0.1484

For the sake of brevity, the cell with the pyrite electrode and that with the platinum electrode will subsequently be called "pyrite cell" and "platinum cell" respectively.

If the pyrite form an "unattackable electrode" whose potential against "water" is raised by an excess of the oxygen content of the

latter, and lowered by that of hydrogen as was Wells's first assumption, the voltages of both pyrite and platinum cells ought to fall or rise simultaneously.

In Exp. No. 16, the pyrite cell gave a voltage of 0.20 at the beginning; it rose gradually until 0.28 volt was reached, while the voltage of the platinum cell made a considerable fall. This, at once, betrays the above assumption of Wells. At about 500 minutes and later, a slight fall in voltage of the pyrite cell could be recognized. This might be ascribed to the effect of the hydrogen in the solution, but the fall of the potential continued for the next two days, although the voltage of the platinum cell was made to go through a considerable rise and fall by the action of the gaseous current.

That the fall of the potential of the pyrite is not due to the polarisation is proved by the increase of the potential in Exp. No. 17, for the conditions of experiment were exactly the same in No. 16 as in No. 17.

In Exp. No. 17, the voltage of the pyrite cell remained nearly constant at 0.17 volt during the first day, while that of the platinum cell changed first from -0.05 to 0.14 volt and then from 0.14 to -0.15 volt, and lastly, from -0.15 to 0.08 volt.

On the next day, the voltage of the platinum cell was also made to change in several ways, but that of the pyrite cell made only a gradual rise until 0.22 volt was reached, where it remained constant.

In Exp. No. 18, the voltage of the pyrite cell went through a slight fall from the beginning till the end of 80 minutes, while that of the platinum cell made an appreciable rise.

In Exp. No. 19, the pyrite cell showed a considerably high voltage, having a tendency to make a slight fall with time, while the voltage of the platinum cell was made to rise gradually.

The platinum electrode has many times assumed a potential of 0.676 volt as are indicated in the table. At these times, (100) of pyrite gave a voltage of ca. 0.834 volt in Exp. No. 16 and 0.835 volt in Exp. No. 18. These stand in good agreement with

each other. But in Exp. No. 17, (210) gave at first ca. 0.737 volt, and afterwards 0.78 volt; while in No. 19, the same kind of crystal face gave 0.89 volt against the "pure water".

In this way, no fixed relation between the potential of the platinum electrode and that of the pyrite was found in the author's experiments, and even the "pure water" was incapable of giving a proper potential for each crystal face which was apparently smooth and shining.

The step-wise change of voltage can not be very clearly recognized in the above tables as the time interval in the measurement was generally large. But still it is not difficult to find certain well marked "steps" of voltage in the tables. Thus, taking rough numbers, 0.283, 0.280, 0.277, 0.270 in Exp. No. 16, 0.177, 0.220 in Exp. No. 17, and 0.276 in Exp. No. 18 may be taken as the "steps".

So far as the above experiments are concerned, therefore, the potential of the pyrite electrode seems to change only at its own will showing several steps, just as in the experiments in the open air.

In the following table, more pronounced "steps" are summarised.

Table 12.
The "steps" of potential (in volt.)

The number of the experiments.														Summary.	Real voltage.	
1	2	3	4	5	6	7	8	10	12	15	16	17	18			
.177				.177			.177		.171						.17	.73
				.190								.177			.177	.737
		.20	.20		.200			.20		.20					.190	.750
								.222							.20	.76
												.220			.221	.781
			.233												.233	.793
			.244												.244	.804
			.247												.247	.807
	.25		.250												.25	.81
												.270			.270	.830
												.277		.276	.277	.837
												.280			.280	.840
												.283			.283	.843

Before we try to make any interpretation of the peculiar phenomena, we have to examine the microscopical surface characters of the crystal faces of pyrites.

Surface Features of Pyrite Crystal.

Of various natural crystal faces of pyrites, those lying in the zone (100)/(110) are most abundant in variety. Thus, Dana gives, in his "System of Mineralogy," 85 different forms as of those observed, of which 37 belong to this zone. These tautozonal faces are various pentagonal dodecahedra, together with cube and rhombic dodecahedron. As is well known, these crystal faces of pyrites are characterised by the presence of "striations" and the latter are due to the oscillatory combination of the facets in the zone (100)/(110) which form the narrow strips of faces elongated in a direction parallel to the zonal axis.

Crystals of pyrite from Udo and Sagi have, of course, these striations besides well defined (hko), (100) and (110) in the zone under consideration. S. Kô¹⁾ has recognized (210), (320) and (410) in addition to (100) and (110) in that zone, employing well defined crystal faces of the samples from Sagi. But it seems to be possible to detect even with a reflecting goniometer, a great many faces of (hko) in more or less finely striated faces. The result of the research into this undertaken by the present author will be reported separately.

Striations are also numerous on (111), and etch-figures are very common especially on (210) and (111), as was described by Kô. Fig. 2 in Pl. XIX represents a photograph from an octahedral face of a sample from Sagi. The face (100) seems to be the smoothest one of all the the crystal faces, but it often possesses small protuberances or flat elevations whose apexes are commonly truncated by (100). Fig. 1 in Pl. XIX represents a photograph from a cubic face, showing the elevations. Some of them are so flat that their presence can only be recognized by means of a microscope of high magnification. The faces (100), (111) and various kinds of (hko) form the margin of these

1) S. Kô, Crystallisation of Pyrite from Sagi. Beiträge zur Mineralogie von Japan. Nr. 3, p. 110 (1907).

elevations as elongated strips of faces the width of which range from fair breadths to submicroscopical fineness.

These macro- and microscopical imperfections of crystal faces afford us a good ground to believe that the same features would prevail also on a surface which is perfectly smooth microscopically, and that which determines the potential against the solution may be quite different in its orientation from the apparent crystal face. The electrical phenomena are presumably concerned with the orientations of these leptonological surfaces and not with those of the rough "forms".

The potential of a crystal face against a given solution may be expected to be different according to its stability against the solution, and the latter, in turn, to be a function of the orientation of the surface in question.

In the case of pyrites, the cubic atom surface seems to be the most stable one among all others especially in the natural underground solutions. This may be inferred from the following facts:

- a) Pyrite has a cleavage parallel to (100) and (111), and that of the (100) is more distinct.
- b) The cubic external form predominates in pyrite crystals from almost all localities, and the natural surface of the cube is mostly smooth and shining.
- c) The face (100) is always predominant in the facets of etch-figures. Some specimens from Udo and Sagi, for instance, possess velvet-like octahedral faces. They are really covered with minute negative trigonal pyramids of (100). Figs. 3, 4 and 5 in Pl. XIX are photographs of the specimens from Udo.
- d) A microscopical examination of crystal edges and corners which are chemically worn down would at one glance reveal the fact that an immense number of thin cubic lamellae are piled up layer upon layer, and we are best convinced with the fact that a pyrite crystal is nothing other than an

accumulation of these thinnest strata which are parallel to (100) just as the piling of thin sedimentary strata would make a rock of a vast thickness.

Surface Density of Free crystalline Bond.

A röntgenographical investigation of the crystal structure of pyrites has revealed that it is composed of face-centered cubic lattice of iron atoms so combined with the same lattice of the S_2 atom groups, that the combined lattices form a simple cubic one the four corners of which, arranged in the positions corresponding to the corners of a tetrahedron, are occupied by iron atoms and the remaining four corners by S_2

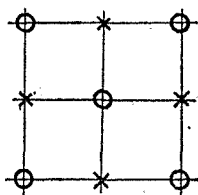


Fig. 2.

○ represents the position of iron atom, and × that of the center of gravity of S_2 -atomgroup.

atom groups.

Then the ideal surface of (100) can be represented diagrammatically as in Fig. 2 in which the positions of the center of gravity of atoms and of atom groups only are marked, the directional character of S_2 atom groups being neglected.

In our analysis of the surface characters of various crystal faces, let us confine our attention first to the crystal faces lying in the zone (100)/(110). Leptonologically considered, all faces in this zone can be constructed by proper accumulation of cubic atom layers. For instance, (110) can be constructed by so piling the cubic atom layers whose straight margins are parallel to the side of the gitter squarelet that the margin of each layer lies exactly one squarelet behind that of the underlying layer. If sheets of paper having straight margins be so piled up that the margin of each sheet comes behind that of the underlying one by a width of the thickness of the sheet, the whole periphery of the pile would form a rough surface whose inclination against the basal surface of the pile is 45° . The construction of (110) face with the sheets of cubic atom layers is geometrically analogous

to the above piling process of paper, the only difference being the thickness of the sheet.

By a similar method of piling, any crystal face having the symbol (hko) may be constructed with the cubic atom layers. Thus, if the straight margin of the second layer be so placed behind that of the first by a width of the thickness of two layers, the third by that of four and the fourth by that of five layers, and the same method of piling of four layers be repeated, the resulting atomic surface will be

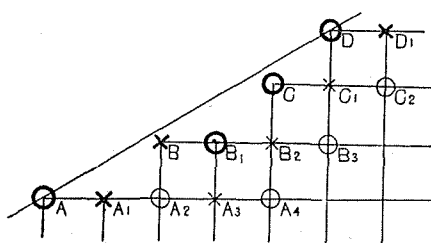


Fig. 3.

○ Position of iron atom.
 × „ „ the center of gravity of S₂ group.

(530). A section perpendicular to the margin of layers in this type of piling is diagrammatically represented in Fig. 3. AD in the figure is the section of the geometrical plane (530).

One can easily see how the actual surface is different from the geometrical plane. An actual surface of (530) can never be more smooth leptonologically than is represented in the figure. It is nothing other than a step-like succession of cubic atom layers each step forming a "striation" parallel to the edge of cube.

Suppose a single chain of atoms which passes through B and is perpendicular to the plane of the paper has disappeared, then we would have a little larger groove whose inner facets are (100) and (110), the former passing through AA₁A₂ and the latter DCB₁A₂. Again, if an atomic chain through C has also disappeared, we would have another facet (520) which passes through AB₁C₁.

In this way, the atomic surface which determines the potential might be very easily renewed by the slightest chemical action of the solution. This will explain the extremely delicate change of the potential of a crystal electrode.

The free surface of the crystal must have been immersed in the underground solution for a vast range of time. In consequence of this,

it must have been engraved by the latter so as to fit the condition of the equilibrium between the two. In certain cases, the fine engravings of this sort are visible to the naked eye, but in many cases they may be so very fine that they are beyond the reach of microscopical detection. This seems to be the most reasonable explanation of the question why the same crystal faces can assume the different potential, and different faces can assume the same potential.

In order to express the relative stability of a crystal face in a numerical measure, the present author wishes to propose a new vectorial measure which can be expressed by a term "surface density of free crystalline bond." This may be taken as the number of "free crystalline bond" distributed in a unit area of the crystallographical face. Here the word "crystalline bond" is to be understood as the direction in which the combining power of an atom (or atom group) with other atoms (or atom groups) exerts itself in the crystal gitter. The "combining power" possessed by an atom in a crystal gitter may be a kind of interatomic cohesion when the crystal is composed of only one kind of atom, or it may consist of cohesion and chemical attraction, the latter exerting its action between negative and positive atoms or atom groups.

Therefore the meaning of "bond" used here may be quite different from the "chemical bond" in the ordinary sense. For instance, the number of bonds possessed by an iron atom is two or three in chemical usage, but it is six in a crystal gitter of pyrite, for an iron atom is surrounded by six S_2 atom groups. In the same manner the bonds possessed by an S_2 atom group in the interior of the crystal body are likewise six in number.

At the surface, however, some of the atoms (or atom groups) may be considered to possess a certain number of free (uncombined) bonds owing to the lack of some of the neighbours. If 1, 2, of the six neighbours be absent, the number of free bonds is 1, 2, respectively. The number of free crystalline bonds thus defined, therefore, represents

the measure of easiness with which the atom (or atom group) in question can be detached from the crystal body and made to go out into the surrounding medium. To illustrate the method of calculation of the "surface density of free crystalline bond," an example is here given.

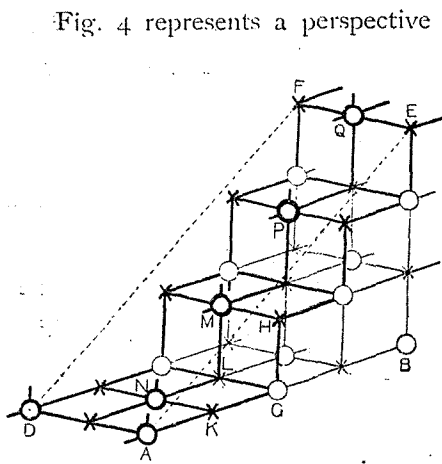


Fig. 4.

○ Position of iron atom.
 × " " the center of gravity of S_2 group.

Among the iron atoms on the surface, those which come actually in contact with the atoms or ions of the solution are distinguished from the others by heavy circles. Any free crystalline bond is possessed only by those iron atoms and by no other iron atoms. The atom G, for instance, is surrounded by six S_2 groups and therefore it has no free crystalline bond. It is buried underneath the two S_2 groups H and K and is protected from the solution.

The number of free bonds possessed by each surface iron atom is figuratively represented by the number of dashes attached to them. As is seen in the figure, seven free crystalline bonds belong to the surface ADFE. If the length of AB be taken as 4, BE=3 and AD=2. Hence the area $ADFE = 2\sqrt{4^2 + 3^2}$. If we denote the surface density of free crystalline bond by D with its suffixes,

$$F_e D_{(430)} = \frac{7}{2\sqrt{4^2 + 3^2}}$$

In general, it is easy to prove that

$$S_2 D_{(hko)} = F_e D_{(hko)} = \frac{h+k}{\sqrt{h^2 + k^2}}$$

if $F_e D_{(100)}$ be taken as unity.

positions of the iron atoms are marked by circles and those of the S_2 atom groups by crosses. Among the iron atoms on the surface, those which come actually in contact with the atoms or ions of the solution are distinguished from the others by heavy circles. Any free crystalline bond is possessed only by those iron atoms and by no other iron atoms. The

By using this formula, the values of D for more important faces of (hko) are calculated. They are given in Table 13.

Potential of (100) of Pyrite in Normal KCl.

The true value of potential assumed by (100) against normal KCl is supposed to be fairly low. Most samples of (100) do not give the true potential owing to the fine engravings caused by the chemical action of the secondary nature.

A specimen having a very perfect cubic surface was obtained with some trial from a little druse in a large mass of pyrite from Udo. That surface looked perfectly smooth and free from all sorts of mechanical and chemical scars. The results of measurements with this face are given in Table 4. By an extrapolation from the potential curve for the same experiment, the reading for the initial voltage is found to be some 0.04 volt. This corresponds to the real voltage of 0.60 volt if the potential of the normal calomel electrode be taken as 0.56 volt, the potential at the liquid contact being really negligible in this case.

R. C. Wells¹⁾ has many times obtained potentials as low as those ranging from 0.6 to 0.8 volt with pyrite electrodes in normal KCl, and as his conclusion, he gives the value of 0.60 volt as the true potential of pyrite. Unfortunately, however, he paid little attention to the surface characters of his electrodes, yet he gives us good ground to believe that this value may be the lowest that a pyrite electrode can assume at the very instant of its immersion in the solution, and therefore it may correspond to the potential of (100). In the following paragraph, the potential of (100) is simply assumed to be 0.600 volt, but this assumption is in no way an unreasonable one.

The Meaning of the Step-wise Variation of Potential.

To elucidate the meaning of the step-wise variation of the potential, we have to introduce two assumptions, namely:

1) R. C. Wells, loc. cit. p. 34-35, 56.

- 1) The potential shown by a cubic surface of pyrite in normal KCl is 0.600 volt, and
- 2) the potential shown by a crystal surface, in general, is proportional to its "surface density of free crystalline bond".

With the above two assumptions, we can calculate the potential of any surface of (hko) in pyrite, for we have simply to multiply $D/D_{(100)}$ into 0.600 volt. The results of such calculations are given in Table 13. For the sake of comparison, more pronounced "steps" of potential which we have already obtained are also mentioned in the same table.

Table 13.

Surface	$D/D_{(100)}$	$0.600 \times D/D_{(100)}$	Steps obtained by measurement.	Difference.
(110)	1.414	0.848		
(870)	1.411	0.846		
(760)	1.410	0.846		
(650)	1.408	0.844		
(540).....	1.406	0.843	0.8430
(430).....	1.400	0.840	0.8400
(750).....	1.395	0.837	0.8370
(850)	1.378	0.826	0.830	
(530)	1.372	0.823	0.81	
(740)	1.364	0.818	0.807	
(210).....	1.341	0.804	0.8040
(320).....	1.325	0.795	0.793-0.002
(730)	1.313	0.787		
(520).....	1.300	0.780	0.781+0.001
(830)	1.287	0.772		
(310).....	1.265	0.759	0.76+0.001
(720)	1.236	0.741	0.737	
(410).....	1.212	0.727	0.730+0.003
(510)	1.155	0.693		
(610)	1.151	0.690		
(710)	1.131	0.678		
(810)	1.116	0.669		
(100)	1.000	0.600		

As is seen in the table, the potentials corresponding to the "steps" agree with remarkable accuracy with the calculated values for the most important surfaces.

It is a well known fact that the atomic surfaces having more simple crystallographical indices have the larger atomic densities, and that the surfaces with larger atomic densities are more stable. This is knowledge derived from experience. It follows directly from this that, when the surface exposed in the solution as the result of etching has happened to have a more simple index, it must persist for a longer time than the other atomic surfaces.

F. Becke¹⁾ has determined the indices of facets developed in the artificial etch-figures of pyrite by optical measurements. According to his conclusion, the facets in the etch-figures are those crystallographical faces which have relatively simple indices and belong to the simple crystallographical zones mostly passing through (100) or (210), the zone (100)/(210) being the most prominent "etch-zone."

A similar result was obtained also by Becke from the observation of natural etch-figures.²⁾

Although Becke's conclusion is concerned only with those rough surfaces which are observable by means of light waves, still it is highly probable that the conclusion is also applicable to the finer etch surfaces. Then it is quite possible that the "steps" of potential should correspond to the atomic surfaces of more simple indices. And as a matter of fact, an excellent coincidence of measured and calculated values can be seen in Table 13. This suggests to us that our assumptions are correct, that is to say, the potential of a cubic atom surface is really 0.600 volt and the potential are in general proportional to the "surface densities of free crystalline bond".

A few steps of potential deviate slightly from those corresponding to the surfaces of simpler indices. The deviations may be due to

1) F. Becke, Aetzversuche am Pyrit. *Tscherm. Min. Pet. Mitt.* Bd. 8, p. 239 (1887).

2) F. Becke, Einige Fälle von natürlicher Aetzung am Kristallen von Pyrit, u. s. w. *loc. cit.* Bd. 9, p. 1 (1888).

experimental error, or they may be an indication of "vicinal faces". However, the step 0.737 volt is a well defined one which was shown by several specimens, though Table 13 gives no explanation of this step.

Here we have to remember that the calculated potentials given in Table 13 are concerned only with one group of surfaces (hko), and that there can exist certain other groups of surfaces belonging to the zones other than (100)/(110).

Becke's measurements with artificial and natural etch-figures show that (102)/(010) and (102)/(111) may also be considered to be etch zones. The atomic surfaces belonging to these zones may show the potentials which do not agree with any calculated values in Table 13. The examination of these atomic surfaces will be postponed for the present; here it is enough for us to confine our attention chiefly to the surfaces lying in the zone (100)/(110), for the latter is the most prominent etch zone in pyrite.

That the etch zone (100)/(110) is the most prominent one is easily recognizable in the gnomonic projections of the observed etch facets given by Becke.¹⁾ The difference in brightness of several natural surfaces of pyrite from Udo or Sagi tells us the same story; the facets in this zone are always bright and smooth while those of the other zones are generally matt and rough.

These facts inform us that the atomic surfaces lying in the zone (100)/(110) are most stable against the action of natural or artificial reagents,²⁾ and hence the atomic surfaces corresponding to most of the steps of potential can be expected to be (hko).

Experiments with Nitric Acid.

Measurements were made in the open air. Nitric acid of 0.2970 normal was allowed to run down slowly in the half cell, the surface

1) F. Becke, loc. cit. Bd. 8, Taf. IV, Fig. 45.

2) The only exception to this general rule is the stability of (111) against the action of free alkalis, but the facets in the zone (100)/(100) are also stable against them. (loc. cit. p. 312).

of pyrite under examination being continually washed thereby. All the arrangements of the apparatus were the same as in the case with KCl solution. Eighteen experiments were made, different specimens being employed for each experiment, but for the sake of brevity, a few examples of the results observed are given in the following tables.

In the tables, readings of the voltage of the total cell are mentioned. Since pyrite always formed the positive electrode, its real potential is to be obtained by adding 0.560 volt to the reading if we neglect the potential difference at the liquid contact.

Table 14.

Exp. No. 21.

Electrode: (III) of pyrite from Sennin.

Solution: 0.2970 normal HNO₃.

Time in minutes.	Reading of potential.	Time in minutes.	Reading of potential.
2.5	0.4088	43	"
4	0.4143	46	"
6	0.4192	48	0.43826
7	0.4222	49.8	0.44491
8.5	0.4262	52	"
10	"	53.6	"
12	0.4280	54.5	"
13	0.4315	56	"
14	0.4330	57.5	"
16.5	0.43507	63	0.44241
18.5	"	64	"
19	"	66	0.44341
20	"	67	0.44540
22	"	67.7	0.44785
23.5	"	70	"
24	"	71.5	"
25.6	0.4357	72.5	"
27.6	0.4361	75	"
29	0.4366	77	"
30	0.4369	78	"
31.5	0.4374	79.5	"
32.8	0.43776	80	"
34	0.43855	81	"
35.5	"	82	"
36.7	0.43878	82.5	"
38	0.43778	85	"
40	0.43405	87	"
40.6	0.43422	88	"
41	"	90	"
42	"		

Table 15.

Exp. No. 22.

Electrode : (110) of pyrite from Udo.

Solution : 0.2970 normal HNO_3 .

Time in minutes.	Reading of potential.	Time in minutes.	Reading of potential.
2	0.35136	42.5	0.33635
4	0.34100	44.5	0.33601
5	"	46.5	0.33609
6.5	0.33615	47.5	"
8	0.33391	48.5	"
9	"	49.5	"
9.5	"	54	"
10	"	56	"
11	"	57	"
12.5	"	59	"
14	"	65	0.33704
16	"	66	"
18.5	"	67	"
19.5	"	68.5	0.33746
20	"	69.5	"
23	0.33510	70.5	0.33781
25.5	0.33609	73	0.33830
26	"	75	0.33855
27	"	78	0.33884
28	"	80	0.33930
29.5	"		
30.5	"		
33	0.33676		
34.5	"		
35	"		
36.5	"		
37.5	"		

Table 16.

Exp. No. 29.

Electrode : (100) of pyrite from Sennin.

Solution : 0.2970 normal HNO_3 .

Time in minutes.	Reading of potential.	Time in minutes.	Reading of potential.
2	0.36284	43	0.42003
7	0.38358	46	0.42057
11	0.39252	51	0.42240
14	0.39742	57	"
19	0.39045	61	0.42835
23	0.40592	65	"
27	0.40805	70	0.43065
31	0.41298	75	"
35	0.41625	79	0.43117
40	0.42003	82	"

Table 16.

Continued.

Time in minutes.	Reading of potential.	Time in minutes.	Reading of potential.
88	0.43485	148	0.44528
95	"	151	0.44565
104	"	156	"
111	"	160	0.44685
115	"	164	0.44792
120	0.43930	167	"
126	0.44000	170	"
133	0.44085	175	"
140	0.44528	181	"
145	"	200	"

Table 17.

Exp. No. 34.

Electrode : (100) of pyrite from Sagi.

Solution : 0.2970 normal HNO₃.

Time in minutes.	Reading of potential.	Time in minutes.	Reading of potential.
0	0.42200	80	0.42000
2	0.42325	85	0.42160
6	"	88	0.42411
10	"	92	0.42645
13	"	95	"
17	0.41473	105	0.42930
23	"	110	"
29	"	116	"
33	"	119	0.42705
35	0.41775	124	0.42490
37	"	126	0.42150
41	"	130	"
50	"	135	"
56	"	140	"
58	"	146	"
60	"	153	"
67	"	155	"
72	0.41950	160	"
75	"		

Table. 18.

Exp. No. 36.

Electrode : (210) of pyrite from Udo.

Solution : 0.2970 normal HNO_3 .

Time in minutes.	Reading of potential.	Time in minutes.	Reading of potential.
6	0.38310	67	0.41820
10	0.38940	72	"
15	0.39840	75	0.41275
21	0.39951	81	0.40735
27	0.40875	84	0.39650
32	"	90	0.38615
36	0.41820	94	0.38400
41	"	104	"
43	"	106	"
45	"	113	0.38900
48	"	115	0.39250
50	"	120	0.39370
56	"	123	"
60	"		
63	"		

The results of experiments with nitric acid are plotted in curves in Fig. 5. As may be seen in the figure, one and the same electrode sometimes shows several "steps" of potential in the course of time just as in the case with KCl solution. Then we have good reason to suppose that the steps may correspond to the different leptonological surfaces.

The "steps" of the potential are summarised in Table 19. In the calculation of the real volages, no attempt was made to make a correction due to the liquid contact.

0.2790 Normal HNO_3

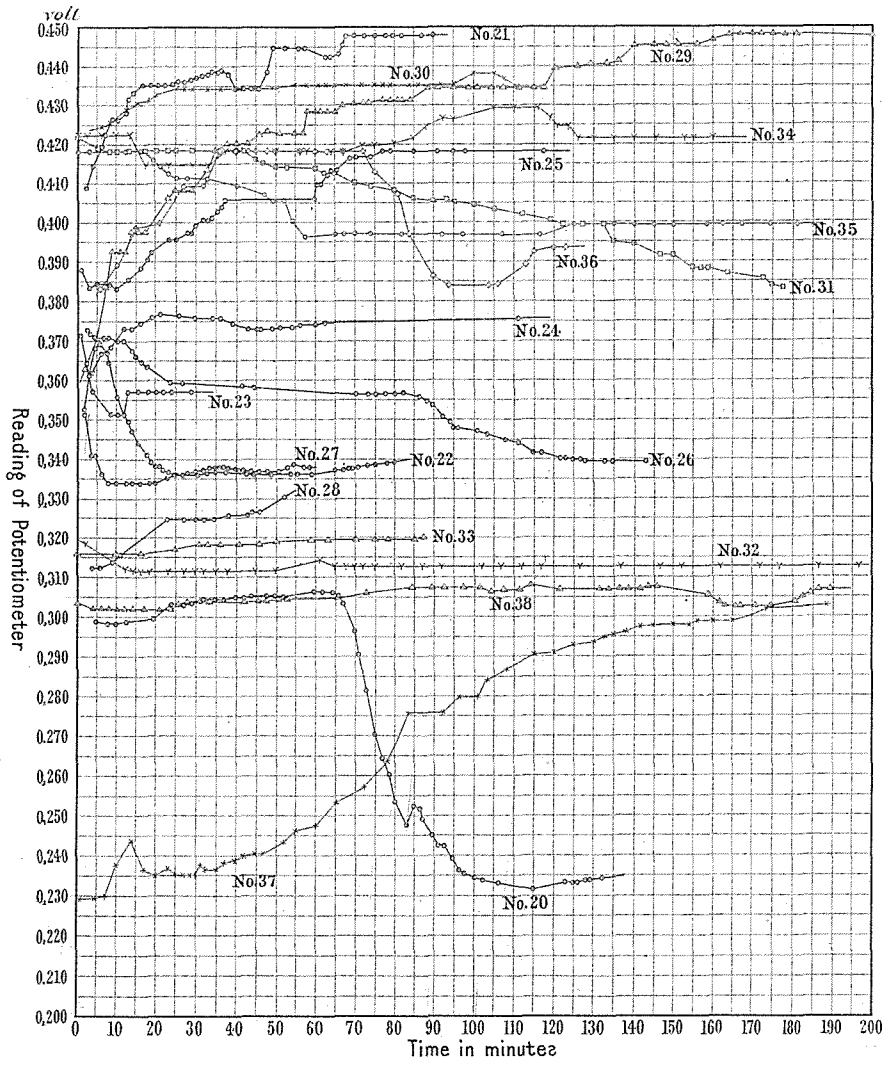


Fig. 5

Table 19.
Summary of "steps"
(Solution: nitric acid.)

Reading.	Real voltage.	Observed in Exp. No.
0.235	0.795	20. 37.
0.305	0.865	20. 38.
0.3116	0.8716	32.
0.3129	0.8729	32.
0.3196	0.8796	33.
0.3245	0.8845	28.
0.3321	0.8921	26.
0.3339	0.8939	22.
0.337	0.897	22. 27.
0.339	0.899	26.
0.3567	(average.) 0.9167	23. 26.
0.375	0.935	24.
0.384	0.944	25. 36.
0.3969	0.9569	35.
0.3991	0.9591	35.
0.418	0.978	25. 31. 35. 36.
0.4215	0.9815	34.
0.434	0.994	21. 29. 30.
0.435	0.995	21. 30.
0.445	1.005	21. 29.
0.4479	1.0079	21. 29.

Becke's observation of the etch-figures in pyrite which were artificially made by the action of nitric acid has shown that the greater part of the facets in the figures belong to the zone $(100)/(110)$.¹⁾ Therefore, we may imagine that most of the steps of potential may correspond to those of pentagonal dodecahedra.

Unfortunately, however, we have no knowledge about the potential of (100) against our nitric acid solution, so it is difficult to make the identification of the steps. To obviate this difficulty the present author

1) F. Becke, loc. cit. Bd. 8, p. 311, (1887).

has contrived a practical method for their identification. The method is as follows :

On a straight line such as AB in Fig. 6, Pl. XIX, the positions of various important faces are so marked that the distance of each mark from a fixed point A on the line is proportional to the corresponding surface density of free crystalline bond. Each position of a crystal face thus marked is connected by a straight line with any arbitrary point such as O in the figure which should preferably be distant from the line AB.

Now, any straight line such as CD which is parallel to AB intersects the connecting lines, and it can be easily proved that

$$Ca' : Cb' : Cc' : \dots\dots\dots = Aa : Ab : Ac : \dots\dots\dots$$

Next we prepare a piece of paper whose two adjacent margins make exactly the same angle as OAB so that if we slide one of these two along the line AO, the other moves always parallel to AB. An example of such a piece of paper is shown by KLMN in the figure.

On the margin MN, we put marks whose distances from M are proportional to the voltages corresponding to the steps. Then we slide the margin ML along AO and examine in what position of the piece its marks coincide with the radial lines from O.

In general, the simultaneous coincidence of many marks with the lines can never happen except only in one case when the piece of paper comes to its proper position. And this was actually found to be the case as is seen in the figure.

We might measure the supposed voltage of (100) by measuring the distance from M to a, but a simple calculation gives a more accurate number. For instance, the figure shows that the mark of 0.9783 volt corresponds to the potential of (530), and since

$$D_{(350)}/D_{(100)} = 1.372,$$

$$E_{(100)} = \frac{0.9783}{1.372} = 0.7130 \text{ volt.}$$

where $E_{(100)}$ stands for the potential of (100).

Using the value of $E_{(100)}$ thus obtained, we can calculate $D/D_{(100)}$ which corresponds to any observed voltage. In the following table, these values are compared with the theoretical ones.

Table 20.

Result with 0.2970 normal HNO_3 .

Steps of potential (volt.)	$E/E_{(100)} = D/D_{(100)}$	$D/D_{(100)}$ theoretical.	Face.	Difference.
0.794	1.186			
0.865	1.213	1.212	(410)	+0.001
0.8716	1.222			
0.8729	1.224			
0.8796	1.234	1.236	(720)	-0.002
0.8845	1.241			
0.8921	1.251			
0.8939	1.254			
0.8970	1.258			
0.899	1.261	1.261	(310)	0
0.9167	1.286	1.287	(830)	-0.001
0.935	1.311	1.313	(730)	-0.002
0.944	1.324	1.325	(320)	-0.001
0.9569	1.342	1.341	(210)	+0.001
0.9783	1.372	1.372	(530)	0
0.9815	1.377	1.377	(850)	0
0.9942	1.394	1.395	(750)	-0.001
0.9950	1.396			
1.005	1.410	1.410	(760)	0
1.0079	1.414	1.414	(110)	0

Since an exceptional coincidence of this kind can never be expected to happen accidentally, our assumption concerning the relation of D to E is also justified here as in the case with KCl solution.

Many steps of potential which do not agree with any theoretical value of $D/D_{(100)}$ for more important faces may represent the faces of larger indices of the same zone, or they may stand for faces belonging to other zones.

Experiment with Potassium Hydroxide.

The solution had a strength of 0.2970 normal. The measurements were made in the open air according to the same method as before. The real values of voltage as well as their variations were generally small, hence a great accuracy in the result can not be expected.

The low voltage suggests that a pyrite crystal, or at least those crystal surfaces of pyrites which belong to the zone (100)/(110), are more stable in alkaline solutions than in acid or neutral solutions. The same result was also obtained by Wells.

The step-wise variation of potential was also observable here. The probable steps are summarised in Table 21.

Table 21.
Result with 0.2970 normal KOH.

Reading of "steps"							
Exp. No.	39	40	41	42	43	Summary.	Real voltage.
		0.171				0.171	0.389
			0.175			0.175	0.385
			0.178	0.178		0.178	0.382
					0.180	0.180	0.380
				0.1853		0.1853	0.3747
	0.19285					0.193	0.367
	0.1955					0.195	0.365
	0.1993	0.1988				0.199	0.361
	0.1997					0.200	0.360
	0.2012	0.201				0.201	0.359
		0.205				0.205	0.355
Face.	(100)	(111)	(111)	(210)	(210)		

The identification of these steps was accomplished by the sliding scale method, from which the supposed potential for (100) was obtained.

Thus

$$E_{(100)} = 0.2729 \text{ volt.}$$

By using this number, the values of D for the observed steps were calculated and compared with the theoretical values as before.

Table 22.
Result with 0.2970 normal KOH.

"Steps" of potential (volt.)	$D/D_{(100)}$ (observed.)	$D/D_{(100)}$ (theoretical)	Face.	Difference.
0.389	1.425			
0.385	1.411	1.414	(110)	-0.003
0.382	1.400	1.400	(430)	0
0.380	1.392	1.395	(750)	-0.003
0.3747	1.377	1.378	(850)	-0.001
0.367	1.344	1.341	(210)	+0.003
0.365	1.337			
0.361	1.322	1.325	(320)	-0.003
0.360	1.319			
0.359	1.316	1.313	(730)	+0.003
0.355	1.300	1.300	(520)	0

Here also we see that the faces of more simple indices determine the steps of potential.

Chemistry of Pyrite Electrode.

It is quite questionable whether a pyrite electrode, under the conditions hitherto described, can be reversible in the most strict sense. During the actual measurement of its potential, which was carried out by the method of compensation, the author tried several times to test whether the measurements give the same result by compensating the potential either from the higher side or from the lower side of it. But both measurements always gave only a difference of a negligible amount. Therefore the measurement could be done with fairly high accuracy. The reason for this will be considered presently.

In order to examine the effect of the concentration of ferrous ions upon the potential, the following experiments were carried out:—

An electrode consisting of a cubic surface of pyrite crystal from

Sennin was immersed in 100 cm. of 0.05 normal oxalic acid, the same apparatus being used as was shown in Fig. 1. To the solution, a little ammonium oxalate was added. A stream of hydrogen sulphide was bubbled into the solution and made always to rub the surface of the electrode.

When the variation of potential had practically ceased, which happened after about 5 hours, a weighed amount of solid ferrous sulphate was added in several steps to the solution, and its effect was observed by the usual method of potential measurement.

Hydrogen sulphide was passed in order to stir up the solution and to keep the ferrous salt from oxidation. In order to reduce the predominating effect of hydrogen ions in the solution, the concentration of the former was sought to be kept as low as possible, but attention was also paid not to allow the concentration of sulphide ions to increase to such an extent as to cause the precipitation of ferrous sulphide.

The concentration of hydrogen ions could be taken as 0.0366 normal if the ionization constant of oxalic acid was 0.1 at the room temperature.¹⁾ If the solubility product of H_2S was 1.1×10^{-23} ,²⁾

$$[S^{=}] = \frac{1.1 \times 10^{-23}}{(0.0366)^2} = 8.2 \times 10^{-21}$$

This was, of course, too small to cause any precipitation of ferrous sulphide, for the solubility product of FeS is, according to Bruner,³⁾ 3.7×10^{-19} . To reduce the concentration of hydrogen ions to a much smaller value, some ammonium oxalate was added to the solution, but still the solution remained clear after the addition of the ferrous salt. Therefore, nearly all the ferrous ions added can be considered to have been kept as such, and consequently the concentration of hydrogen ions suffered no change during the experiment.

The results are tabulated as follows:

1) Y. Osaka, Physical Chemistry, 3rd. Ed. p. 286 (1917).

2) J. Knox, Zur Kenntniss der Ionenbildung des Schwefels, etc. Zeitschr. f. Elektrochem. Vol. 12, p. 481 (1906).

3) W. Lewis, A System of Physical Chemistry. Vol. 1, p. 320 (1920.)

Table 23.

Exp. No. 44.

Electrode : (100) of pyrite from Sennin.

Initial composition of the solution : 0.05 normal oxalic acid containing a little ammonium oxalate, the solution being always saturated with H_2S .

Positive pole of the cell : calomel electrode.

Time in minutes.	Reading of potential.	Time in minutes.	Reading of potential.
3	0.09950	346	0.18743
5	0.12302	360	0.18932
7	0.13727	369	0.19100
9	0.14471	377	"
16	0.15990	395	"
21	0.16311	0.2488 gram of $FeSO_4 \cdot 7H_2O$ is added.	
24	0.16635		
31	0.17067	410	0.17145
148	0.18313	413	0.17084
169	0.17862	415	0.16956
175	0.17914	446	"
201	0.18406	461	"
218	0.18654	476	"
233	0.19131	Left standing overnight.	
270	0.19236		
284	"	1350	0.161
310	"	1485	0.16776
0.0054 gram of $FeSO_4 \cdot 7H_2O$ is added.		1505	0.17210
324	"	1595	0.17820
0.0278 gram of $FeSO_4 \cdot 7H_2O$ is added.		1715	0.18910
336	0.18976	1775	0.19223
341	0.18743	1800	"

Note: The ferrous salt added used to remain undissolved for some time especially after the addition of a large amount of it, but it was gradually brought into solution by the stirring action of H_2S .

As is seen in the table, the potential of pyrite suffered no change after the first addition of the ferrous salt. After the second addition, a slight rise of potential was observed, but the initial value was soon

recovered. After the third addition, the rise of potential was conspicuous, but after about eight hours' passage of H_2S the potential fell to the initial magnitude, and remained constant afterwards.

The higher potential was apparently due to the ferric-ferrous potential, for, as was proved by the precipitation of free sulphur in the solution, the ferrous salt added was not free from ferric salt.

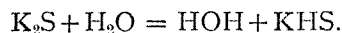
According to the well known research of Peters,¹⁾ the ferric-ferrous potential can be zero only when the ratio of ferro to ferri ions has reached over 10 million. So great purity of the reagent can not be expected in the ordinary materials of laboratory use. So it is quite reasonable that the ferric ferrous potential should make its appearance especially after the addition of a large amount of the salt.

In short, the concentration of ferrous ions as well as of sulphate ions do not seem to have any great effect upon the potential of a pyrite electrode under the above conditions. The same result was obtained by Wells with a marcasite electrode in a dilute solution of sulphuric acid saturated with H_2S . He adds:

“.....This was proved by measurements upon marcasite, but the results would probably have been similar for pyrite”.

And this presumption of Wells is fully proved here.

In cases when the solution consists either of acid, alkali or neutral alkali salt, the formation of a little hydrogen sulphide or alkali sulphide is possible. Then the electrical phenomena may be ascribed chiefly to the action of these sulphides. But hydrogen sulphide is, after all, a very weak acid and its alkali salt must be largely hydrolysed especially in a dilute solution according to the equation:



In order to examine either $S^{=}$ or SH^{-} was the true carrier of electricity, the following experiment was carried out:—

A solution of neutral sulphide of a known concentration was made

1) R. Peters, Über die Oxydations und Reduktions kette. Zeitschr. f. phys. Chem. 26, 193 (1895).

to run down upon a pyrite electrode consisting of a cubic surface of pyrite from Sagi, and the potential was measured in the air as usual. After the potential had practically "settled", the concentration of the running solution was altered and the measurements were continued, and so on. The results are shown in Table 24.

Table 24.

Exp. No. 45.

Electrode : (100) of pyrite from Sagi.

Temperature : 18° C.

Time in minutes.	Potential of pyrite —0.560. volt.	Time in minutes.	Potential of pyrite —0.560. volt.
a) Solution normal Na ₂ S.			
1	—0.76515	38	—0.75865
4	—0.75985	40	—0.75915
6	—0.75899	41	—0.75956
7	"	42	"
9	—0.75660	43	—0.76035
12	—0.75286	44	"
13	—0.75095	46	"
15.5	—0.74855	47	"
17	—0.74716	48	"
21	—0.74800	49	—0.76000
25	—0.75114	50	"
27	—0.75431	51	"
28	—0.75580	52	"
29	"	53	"
30	"	54	"
31	—0.75651	55	"
32	—0.75739		
33	"		
b) Solution : 0.64 normal Na ₂ S.			
1	—0.73912	19.5	—0.74645
2	—0.74125	22	—0.74670
3	—0.74221	24	—0.74747
4.5	"	29	—0.74814
11	—0.74403	33	—0.74890
13	—0.74472	48	—0.74933
16.5	—0.74410	58	"
18	—0.74587		
c) Solution : 0.512 normal Na ₂ S.			
1	—0.74145	12	—0.74462
3	—0.74580	21	"
4.5	—0.74524	24	"

Table 24.

Continued.

Time in minutes.	Potential of pyrite -0.560. volt.	Time in minutes.	Potential of pyrite -0.560. volt.
d) Solution : 0.4096 normal Na ₂ S.			
1	-0.73045	5	-0.73900
2	-0.73880	10	-0.73936
3	-0.73818	16	-0.73860
e) Solution : normal Na ₂ S.			
1	-0.75635	3	-0.75939
2	-0.75835	4	-0.76000

In this group of measurements, sufficient time was not given to each series of measurement, so it is quite questionable whether the potential has completely "settled" at the end of each series. Therefore we can not hope to make any exact calculation from the above data, but as a whole, enough constancy of potential was attained in each series to examine the result qualitatively. The last series of measurements shows that the surfaces of the electrode had suffered no change in its surface features during the whole experiment.

We may summarise the above results as follows :—

Table 25.
Summary of Exp. No. 45.

Concentration of solution.	Ratio of concentration.	Potential - 0.560 volt.	Difference in potential.
1	0.8 ⁰	-0.76000	
0.64	0.8 ²	-0.74933	0.01067
0.512	0.8 ³	-0.74462	0.00471
0.4096	0.8 ⁴	-0.73860	0.00602
			Sum. 0.02140

The average difference of potential corresponding to the change of concentration from x to $0.8x$ is

$$\frac{0.0214}{4} = 0.0054 \text{ volt.}$$

Now let us consider an imaginary cell consisting of two electrodes exactly similar to those used in the above experiment, the one being immersed in a sodium sulphide solution of concentration x , the other in one of the concentration $0.8x$. If the two solutions are connected by means of a suitable wick, the whole would make a concentration cell whose voltage measures about 0.0054 volt. If we close the external circuit of the cell, current will flow from the concentrated to the dilute solution through the wick, or, what amounts to the same thing, the anions will move from the dilute to the concentrated solution.

The voltage of a concentration cell in general can be expressed by the well known equation

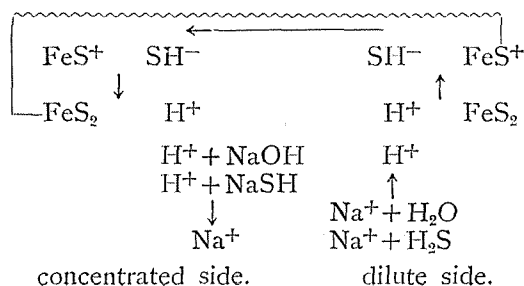
$$E = \frac{RT}{nF} \ln \frac{C_1}{C_2}$$

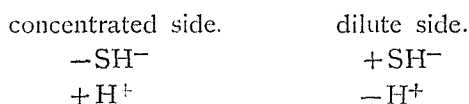
where C_1 denotes the concentration of the electrochemically active ion in the concentrated solution, while C_2 that in the dilute solution, n denoting the valency of that ion. In our case, the ions that are concerned with the electrical phenomena are certain anions.

Since the temperature was kept at 18°C., the voltage of our concentration cell may be calculated from the above equation under an assumption that the electrode was practically reversible. Thus

$$E = \frac{1.987 \times 291 \times 4.189 \times 2.303}{n \times 96540} \times \log \frac{1}{0.8} = \frac{0.0055}{n} \text{ volt.}$$

This suggests at once that the value of n is unity, that is to say, the anion which carries the electricity is really SH^- ion and not $\text{S}^{=}$ ion. Then the mechanism of the production of electricity in the above cell may be expressed by the following diagram :—

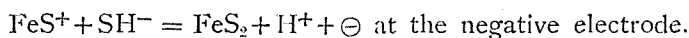
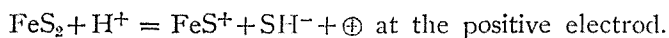




At the positive electrode, a H⁺ ion attacks one of the sulphur atoms of FeS₂ and forms an SH⁻ ion imparting to the electrode a positive charge. The SH⁻ ion thus produced will migrate away from the electrode carrying a negative charge; it will react with FeS at the negative electrode to form FeS₂ and a H⁺ ion imparting to the electrode a negative charge. The H⁺ ions thus produced will migrate directly toward the positive electrode when the solution contains no alkalion, but they can expel the alkalions around the electrode if the latter be present.

If alkalions be present in the solution, they will produce hydrogen ions at the positive electrode just as in the case of the electrolysis of water. Therefore, the presence or absence of alkalions make little difference in the general scheme of the production of electricity.

During the flow of a unit amount of current, one gram-ion of SH⁻ is consumed and one gram-ion of H⁺ is produced at the negative electrode, while at the positive electrode, the relation is reversed. Expressed in chemical equations,



The above diagram gives a very simple and easy explanation of the observed phenomena. If the solution consists of an alkali sulphide, SH⁻ ions predominate in the solution, hence the condition corresponding to the concentrated side of the above diagram prevails and the solution is positively charged against the electrode. However if the solution consists of an acid, H⁺ ions predominate in the solution, and consequently the electrode is positively charged against the solution corresponding to the condition of the dilute side.

The production of FeS⁺ might be regarded as a peculiar assumption, but a simple consideration of the surface characters of pyrite will give a clear answer to it.

Hitherto we have considered, for the sake of simplicity, only the center of gravity of the S_2 group and not the actual positions of the sulphur atoms. This was really sufficient for our analysis of the surface stability because we have had only to enumerate the number of S_2 groups exposed on the surface. One of the two sulphur atoms, which form a small doublet in the crystal gitter, is more or less deeply buried underneath the surface layer of iron atoms as well in all pentagonal dodecahedra as in a cube, and is not easy to be attacked by the solution, while the other is exposed more or less high above the level of the surface layer of iron atoms and occupies an unstable position.

In the case of (110), one half of the total number of the surface S_2 groups are so placed that the two atoms in each sulphur doublet are placed on the surface plane of iron atoms. But even in this case it is better to consider that only one of them enters the chemical reaction, for, should the two be carried away into the solution at the same time, an endless decomposition of crystal gitter would ensue.

From the chemical standpoint, too, it is quite natural to consider that a persulphide should lose one of the two sulphur atoms at the first step of its decomposition.

In the case of the decomposition of such a compound as H_2O_2 , the positions of each of the hydrogen and oxygen atoms can be easily adjusted so as to form a neutral H_2O molecule after the decomposition. In a crystal surface, however, the positions of atoms and their "orientations", if any, are more fixed so that the adjustment to form a neutral molecule of FeS would not be easy. For example, after the removal of one atom of sulphur from the doublet on the cubic surface, the remaining one can not move to the position of the center of gravity of the original doublet so as to form a neutral FeS on the surface for its position is fixed by its relation with the inside iron atoms.

Therefore, it is not unreasonable to express the reaction product

on the surface as positively charged FeS although it is not a free ion, but a part of crystal body.

If there be enough FeS and FeS₂ on the surface of the electrode in the double layer condition so that the flow of a small amount of current can not consume FeS or FeS₂ on the surface, the electrode may be reversible. In order to realise this condition, either the electrode should have an immense area or the current should be negligibly small. From the practical standpoint, the latter condition is easier to be realised as a careful compensation would reduce the current to the minimum. The facet that the compensation can be accomplished either from the higher side or from the lower side of the real voltage with practically the identical result comes in consonance with the above reasoning.

Local Current as the Result of Surface Features.

The voltage of a local current is determined partly by the nature of the impurity in the substance of the electrode; but it must be noticed that the difference in the surface features of the crystal grains of the electrode may be a potent factor in the production of a local current. For instance, if, on a surface of a pyrite crystal, which is immersed in normal KCl solution, two atomic surfaces (430) and (410) happen to exist, a local current ought to be produced whose voltage measures.

$$0.840 - 0.730 = 0.110 \text{ volt.}$$

This is by no means a small voltage. A current will at once flow from the surface (430) to that of (410) through the crystal body, and consequently sulphur atoms on the surface (430) must go into the solution and SH⁻ ions should discharge at the surface of (410). If the solution be constantly stirred up so as to prevent the polarization, the decomposition of (430) will rapidly proceed, and it will continue until the latter is reformed to (410). If, for some reason, (410) is not produced and (100) be exposed instead, a current will flow in the

reverse direction from the instant of its appearance. The voltage of this current will be 0.130 as is easily calculated from Table 13.

A surface of a mass of pyrite consisting of many crystals of different orientations, in general, can not be expected to expose the similar atomic surface everywhere. So the local current will flow from the most labile surface toward the most stable one through the mass when the latter is immersed in a solution. From a surface of a certain intermediate stability, currents will tend to flow toward the more labile surfaces through the solution, but at the same time currents will flow toward that surface from the more stable ones through the solution. These two opposite effects will cancel each other, or one of them may be reduced by the other to a small voltage.

Conditions will be the same if two masses of pyrite be connected by a conducting wire and immersed in the solution. If the most labile atomic surface be situated in one mass, and the most stable surface in the other, the system will make a cell in which the two masses of pyrite form the electrodes and the connecting wire serve as the external circuit.

This seems to give a good explanation of certain electrochemical phenomena which have hitherto not been completely elucidated. To give an example of such a phenomenon, the following lines are quoted from Lewis's "Physical Chemistry".¹⁾

"According to Newbery a strip of sheet copper cleaned and cut into two pieces will give, when these pieces are connected to a micro-ammeter and immersed in CuSO_4 solution, a gradually decreasing current for two or three days. This procedure of shortcircuiting the two (apparently identical) electrodes is always resorted to before setting up a concentration cell in order that the metal may be as far as possible in the same state. Some process occurs in the surface layer which may possibly be a kind of surface crystallisation of the metal or the orientation of the atoms in the surface as the result of slight electrolysis".

1) W. Lewis, A System of Physical Chemistry. Vol. II, p. 146 (1920).

The phenomenon observed by Newbery is just the same as in the case of a cell with two pyrite electrodes which was illustrated above. As long as the most labile and the most stable surfaces exist in different sheets, a noticeable current will flow through the external wire. If, however, the two kinds of surfaces happen to exist in the same sheet in Newbery's experiment, the current would have been very small, for the solution, the other sheet and the external wire would have formed only a shunt circuit of a larger resistance.

Therefore the decay of the current observed by an ammeter does not necessarily mean that the local current has completely ended; it may still continue to flow within one and the same sheet.

Summary and Conclusion.

1) The potential of a pyrite electrode is proportional to the "surface density of the free crystalline bond" of the surface in action, and since the latter is determined by the crystallographical indices of that surface, we can, at least to a certain extent, compute the index from the observed value of the potential.

2) The actual surface which determines the potential is often different from the apparent one. Moreover, the former is changed by the action of the solution with consequent change of the potential. This change of the actual surface continues until some stable surface is exposed, in which case the velocity of the variation of the potential becomes very small.

3) The variation of the potential occurs in a discontinuous manner; many specimens show more than one period during which the potential remains unchanged. The potentials at these periods correspond to those of more or less stable atomic surfaces of simpler indices. Therefore the fundamental nature of these fine facets is the same as that of those which are observable in the etch-figures by optical means.

4) The extreme delicacy in the change of the finest atomic skin due to the circumstances gives a good explanation of the uncertainty

of the potential not only of a pyrite electrode but presumably also of other electrodes of crystalline nature.

5) The potential difference between a pyrite electrode and a solution is the result of an accumulation of SH^- ions around the electrode as the sequence of the reaction of H^+ ions with the sulphur atoms when the electrode assumes a positive charge against the solution; when the electrode is more negatively charged than the solution, it is the result of the reaction of SH^- ion upon the surface of the electrode and the consequent accumulation of H^+ ions around it.

6) When a pyrite is immersed in a solution, a local current may be produced.

a) by the local difference in the surface of a crystal;

b) by that of a mass of crystal grains;

c) by that of two masses connected by some conducting body; etc.

In the case of pyrite, the voltage of these small "elements" can be computed, at least to a certain extent, from the indices of the surface in action.

This research work was accomplished at the expense of the fund for scientific investigations supplied by The Department of Education in the

Mineralogical Laboratory,

Kyoto Imperial University.

July 28, 1924.

Explanation of Pl. XIX.

Fig. 1. A cubic face of pyrite from Udo, showing protuberances of lamellar structure. Magnified 2 diameters.

Fig. 2. An octahedral face of pyrite from Sagi, showing numerous striations. Magnified 2 diameters.

Fig. 3, 4 and 5. Pyrite specimens from Udo, showing rough octahedral faces. They are really covered with minute cubic facets from which a simultaneous reflection of light can be obtained. Magnified 2 diameters.

Fig. 6. The sliding scale used in identification of the "steps of potential." The figure represents the result of the experiment with nitric acid. Contracted to ca. 1/10 diameter.

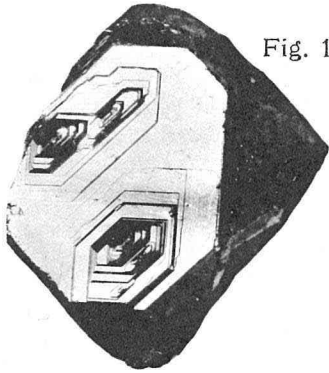


Fig. 1

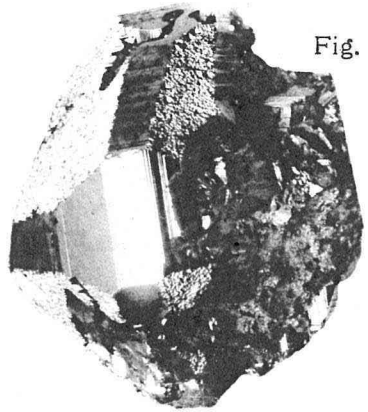


Fig. 5

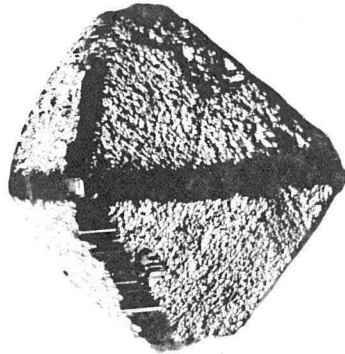


Fig. 3

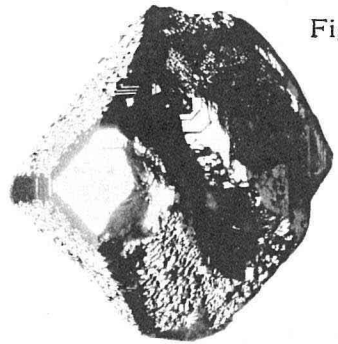


Fig. 4

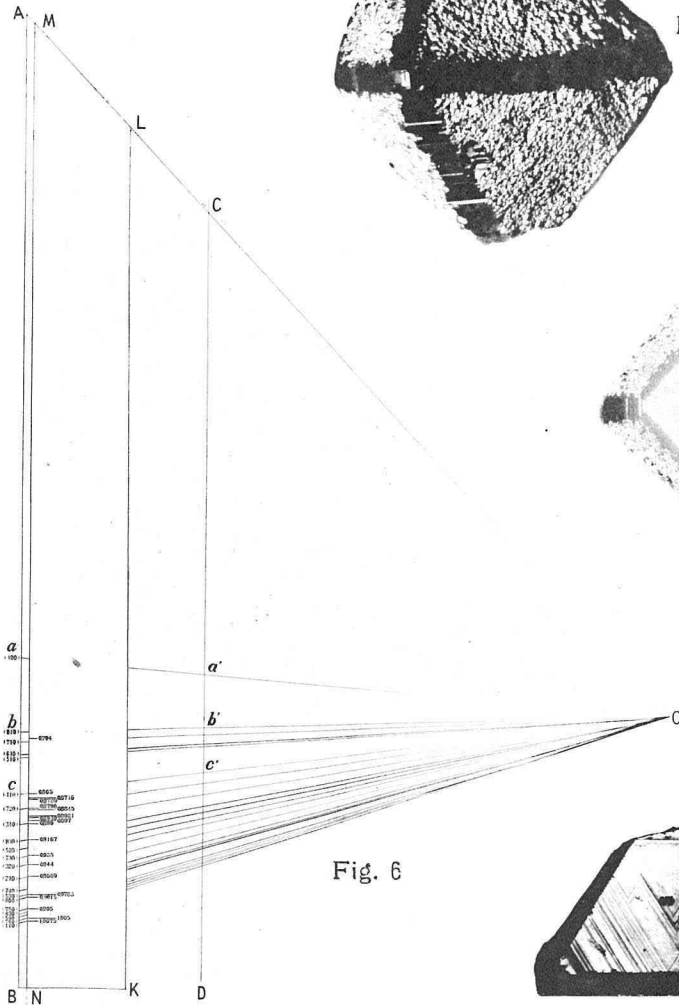


Fig. 6

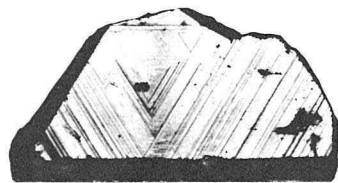


Fig. 2