The work of Bodenstein and Ohlmer on the reaction between carbon monoxide and oxygen is also in quantitative agreement with the new theory. Other cases, including several studied experimentally in this laboratory, will also be discussed.

Summary.

1. The velocity of the reaction by which hydrogen is dissociated in contact with a heated tungsten wire is so enormous that it definitely proves that the reaction cannot depend upon a diffusion of hydrogen into the metal even if the depth of penetration should be only that of a single atom.

2. A general theory of heterogeneous chemical reactions is outlined in which the reaction is assumed to take place in the actual surface layer of atoms.

3. This theory is worked through in detail for the case of the dissociation of hydrogen. It leads to equations which become identical with that previously derived by other methods, when it is assumed the hydrogen evaporates so rapidly from the surface that only a negligible fraction of the surface is covered at any time. This equation has already been shown to be in full agreement with the experiments (Parts I and II).

4. The conclusion that very little of the surface is covered is in good accord with the fact that the accommodation coefficient of hydrogen is 0.19 at temperatures below 1500° K., while the "chemical" accommodation coefficient α_2 for the dissociation of hydrogen is 0.68 at high temperatures.

5. The fact that the electron emission from heated tungsten is not affected by the presence of pure hydrogen is additional evidence that the fraction of the surface covered by hydrogen atoms or molecules must be very small.

ACCURACY OF COPPER VOLTAMETERS.

BY ASWINI KUMAR DATTA AND NILRATAN DHAR.

When a current of moderate strength is to be measured by the copper voltameter the results given by it agree with those obtained from the silver voltameter of Rayleigh's form[1] improved upon by Richards[2] and his pupils. Richards considers that the improved silver voltameter can be relied upon to one part in ten thousand or more. The silver voltameter is therefore a very good register of current and we are quite justified in judging the accuracy of a copper voltameter by comparing its results with those of the standard silver voltameter. When very feeble currents are mea-

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[1] *Phil. Trans.*, **175**, II, 411 (1884).
[2] *Z. physik. Chem.*, **32**, 321 (1900).

sured by the copper voltameter it is found, as a rule, that the values obtained from it are lower than those obtained from the standard silver voltameter. With a view to remove these difficulties and to find the probable causes of the inaccuracy this investigation was undertaken.[1]

The arrangement of the apparatus was as usual. The street main was used as the source of current. A liquid resistance was put in the circuit, which was adjusted till the milliameter used indicated the desired current. The surface of the copper cathode was 6 sq. cm. A slow current of carbon dioxide was bubbled through the solution in the voltameter. The current was generally passed for $2^1/_2$–$3^1/_2$ hours, after which the copper cathode and the platinum bowl with their deposits were carefully washed, dried and weighed. It was noticed incidentally that the silver nitrate solution used in the platinum bowl lost in strength after a few days' use, probably due to partial reduction from organic matters, when the silver deposit would become loose and so the solution had to be changed from time to time in order to get a compact deposit which could easily be washed without any loss of silver deposit.

The solution generally used in the copper voltameter is that indicated by Oettel,[2] which is as follows: 150 g. copper sulfate, 50 g. sulfuric acid, 50 g. alcohol, 1000 g. water. First of all we tried the effect of adding sulfuric acid to the solution. 18.75 g. of recrystallized copper sulfate were dissolved in 125 cc. water (Oettel's quantity) and gradually added small quantities of acid (sp. gr. 1.745). The current was kept constant and was 10 milliamperes. The current density is therefore 0.0017 ampere *per sq. cm.*

TABLE I.—RESULTS OF EXPERIMENTS.

Acid added. Cc.	Silver deposit.	Copper deposit.		Error. Per cent.
		Found.	Calculated.	
o	....	....	.....	Cu electr. blackened.
0.5	0.0873	0.0228	0.02572	11
1	0.0834	0.0226	0.02458	8
2	0.0958	0.0261	0.02823	7
3	0.0633	0.0174	0.01865	6.7
4	0.0958	0.0263	0.02823	6.9
5	0.0769	0.0208	0.02266	8.2

Thus it is found that small addition of sulfuric acid improves the result. The best effect is produced by the addition of 3–4 cc. of the strong acid in 125 cc. of the solution. Oettel's quantity 3.6 cc.

The current strength was now varied to find the range in which we can get good results by using a solution of copper sulfate and sulfuric acid only.

[1] Cf. *Dhar, Z. Elektrochem.*, **19**, 746 (1913).

[2] *Chem. Ztg.*, **17**, 543, 577 (1893).

TABLE II.

Current density.	Silver deposit, g.	Copper deposit.		Error. Per cent.
		Found, g.	Calculated, g.	
0.0033	0.1872	0.0550	0.05513	0.25
0.0025	0.1684	0.0486	0.0496	2.0
0.0013	0.0805	0.0207	0.0237	12
0.0011	0.0492	0.0126	0.0145	13
0.0007	0.0440	0.0107	0.0129	17
0.0003	0.0308	0.0068	0.0091	27

It is evident from the results of Table II that with current densities above 0.0025 ampere per sq. cm. we get accurate results even without using alcohol. As the current density falls the inaccuracy increases rapidly and reaches as much as 25% with a current density of 0.0003 ampere per sq. cm. With alcohol we get much better results but they are still unsuited for accurate work.[1] We now tried for obtaining a better substitute for alcohol and experimented with various substances. As a result of this we found that cane sugar and glucose can serve the purpose of alcohol equally well and that tartaric acid is a decidedly better substitute as the following results will show. During the course of these experiments the current was kept fairly constant and was about 7 milliamperes, the current density being about 0.0011 ampere per sq. cm.

TABLE III.

Cane sugar added. Grams.	Silver deposit, g.	Copper deposit.		Error. Per cent.
		Found.	Calculated.	
0.0	0.0805	0.0207	0.02372	13.0
2.0	0.0731	0.0195	0.02154	9.5
4.0	0.0788	0.0219	0.02322	5.6
6.3	0.0819	0.0231	0.02413	4.3
8.5	0.0742	0.0211	0.02186	3.5
10.6	0.0908	0.0261	0.02676	2.5
14.0	0.0746	0.0217	0.02198	1.7
16.0	0.0706	0.0205	0.02080	1.4
21.0	0.0649	0.0188	0.01912	1.7
30.0	0.0858	0.0239	0.02528	5.0

The results decidedly improve with the addition of cane sugar. The best results are obtained when 15–20 g. of sugar are added per 125 cc. solution. With alcohol results of similar accuracy are obtained.[2]

TABLE IV.

Glucose added. Grams.	Silver deposit, g.	Copper deposit.		Error. Per cent.
		Found.	Calculated.	
2	0.0852	0.0230	0.02511	8.0
5	0.0772	0.0219	0.02275	3.7
8	0.0913	0.0262	0.02690	2.6
10	0.0746	0.0215	0.02198	2.2
14	0.0694	0.0200	0.02045	2.2
15	0.0821	0.0236	0.02419	2.4

[1] Z. Elektrochem., 19, 746 (1913).

[2] Ibid., 19, 746 (1913).

Here also we find glucose to have almost similar effect. The quantity required is about half that of cane sugar, as might be expected from its molecular weight.

TABLE V.

Tartaric acid added. Grams.	Silver deposit. g.	Copper deposit.		Error. Per cent.
		Found.	Calculated.	
0.0	0.0795	0.0201	0.02343	12.4
2.0	0.0744	0.0204	0.02192	6.8
4.8	0.0537	0.0149	0.01582	5.7
6.8	0.0750	0.0211	0.02210	4.7
9.0	0.0798	0.0226	0.02351	3.8
11.0	0.0693	0.0198	0.02042	2.9
13.0	0.0907	0.0260	0.02673	2.7
18.0	0.0858	0.0248	0.02528	1.9
23.0	0.0970	0.0283	0.02858	1.0
25.0	0.0981	0.0287	0.02891	0.73
28.0	0.0635	0.0186	0.01871	0.59
32.0	0.0967	0.0280	0.02849	0.98

Here we have a decided improvement. With the addition of only 2 g. of tartaric acid the error falls from 12% to 7% and then it gradually diminishes with the increment of tartaric acid added. With the addition of 20–35 g. of tartaric acid the error is less than one per cent.

Under these conditions we tried to vary the concentration of copper sulfate but found that Oettel's concentration gave the best results.

Now we substituted hydrogen for carbon dioxide. The experiments were carried out in a closed cell. The voltameter cell was closed with a cork fitted with two glass tubes. Through one tube a slow current of hydrogen, after being passed through two wash bottles containing potassium permanganate solution and pure water, respectively, was bubbled and the other served as an exit tube for the gas.

TABLE VI.—PASSING HYDROGEN THROUGH ELECTROLYTE.

Silver deposit, g.	Copper deposit.		Error. Per cent.
	Found.	Calculated.	
0.0924	0.0270	0.02722	0.8
0.0938	0.0275	0.02774	0.9
0.1416	0.0414	0.04173	0.7

No decided improvement is observed here by using hydrogen for carbon dioxide and using a closed cell and the error is as before about 1%.

The experiments were now conducted at about 0°. The closed cell was surrounded by ice.

ELECTROLYTE AT 0°.

Silver deposit, g.	Copper deposit.		Error.
	Found.	Calculated.	
0.0854	0.0252	0.02517	Practically nil
0.1382	0.0406	0.04073	
0.1013	0.0299	0.02985	

Summary.

From the above investigation we arrive at the following results:

It is immaterial whether we conduct the experiments in an atmosphere of carbon dioxide or hydrogen. Their function is only to exclude air and hence prevent the access of oxygen into the voltameter.

Sulfuric acid is essential for ensuring a good result. It prevents the hydrolysis of the copper sulfate solution, which would cause a deposition of cuprous and cupric oxide on the cathode. It also diminishes the concentration of the copper ions in the solution, due to the increase of SO_4'' ions and also due to the formation of complex copper salts as indicated by the equation[1]

$$H_2SO_4 + CuSO_4 \longrightarrow H_2Cu(SO_4)_2.$$
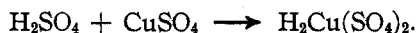
Cane sugar and glucose can be substituted for alcohol with equal efficacy and tartaric acid is a decidedly better substitute and with it we can get good results even with feeble current strength.

It has been observed by Foerster and Seidel,[2] Abel and others that copper sulfate solution appreciably dissolves copper and this dissolution depends greatly on the concentration of copper ions in the solution, and also on the temperature, higher temperature favoring the dissolution. The action is more pronounced in presence of sulfuric acid which we add to prevent hydrolysis. In measuring high currents this does not materially effect the results of the experiments as the copper deposition is rather rapid, while in case of measuring feeble current the copper is deposited very slowly and the copper sulfate solution finds sufficient time to dissolve it appreciably. The dissolution of copper in this way can be very much lessened by diminishing the concentration of the copper ions in the copper sulfate solution. The improvement made by the addition of tartaric acid is probably due to its forming a very good complex with copper ions and thus diminishing the concentration of the copper ions. Functions of alcohol, sugar and glucose are probably the same as they are also known to form complexes with copper salt. This dissolution of copper is hampered by fall of temperature and so we got better results by surrounding the voltameter with ice. The low temperature also diminishes hydrolysis. But here also we have a limit. We cannot measure extremely feeble currents with fair accuracy, for in this case the deposit of copper is so very slow that the small concentration of copper ion evolved from the complex is sufficient to vitiate the result though very slightly by dissolving a little of the freshly deposited copper.

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[1] Cf. Gray, *Phil. Mag.*, **22**, 400 (1886).

[2] *Z. anorg. Chem.*, **14**, 106 (1897); Abel, *Ibid.*, **26**, 1901.