

# ELECTROLYTIC SOLUTION PRESSURE OF COPPER WIRES UNDER STRAIN

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It is long since known that the tension existing on the surface of the metals has a considerable influence on the potentials of the metals in solution of its salts and therefore it has been found necessary to fix definite conditions for the preparation of the electrodes.

Uptil now no systematic study has been undertaken to establish a relationship between these strains and the electrolytic solution pressures. This is clearly due to the fact that strains are difficult to measure. The solitary instance of an attempt to study the effect is by M. G. Moore<sup>1</sup> who had done experiments to determine any change in the energy of emergence with change in the state of strain of the metal surface. The difference between the energy of emergence of the strained and unstrained surfaces was measured by the difference in the contact potential. His experiments showed that with an expansion of 1% the change in the energy of emergence was certainly less than  $4 \times 10^{-3}$  volts. His experiments were not intended to investigate any relation between strain and electrolytic solution pressure and therefore are of little use.

The experiments mentioned herein are an attempt for a systematic study of P. D. between strained and unstrained metallic surfaces dipping in solution of a metallic salt. As a result it is found that molecular aggregation on the surface of the strained wires plays an important part in the values of potential differences.

For the purpose of these experiments two copper wires were annealed by heating them till red hot and then dipping in methyl alcohol. This treatment has been found to give reversible copper electrodes. An electrolytic cell was prepared as shown in Fig. 1, one of the wires marked A was loose and without any strain while the other wire B was strained by suspending weights.

The cell C was filled with copper sulphate solutions of definite and known strength. An E.M.F. was found to develop between the strained and unstrained wires. The galvanometer used was a suspended coil mirror type made by Cambridge Instrument Co., Ltd., England, and had a sensitiveness giving 1 m.m. deflection for a current of  $4 \times 10^{-9}$  amp. The

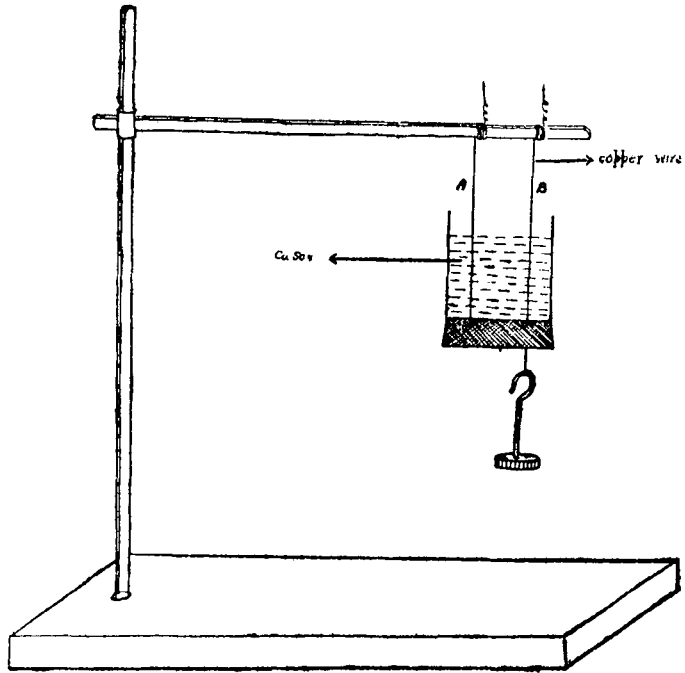


FIG. 1

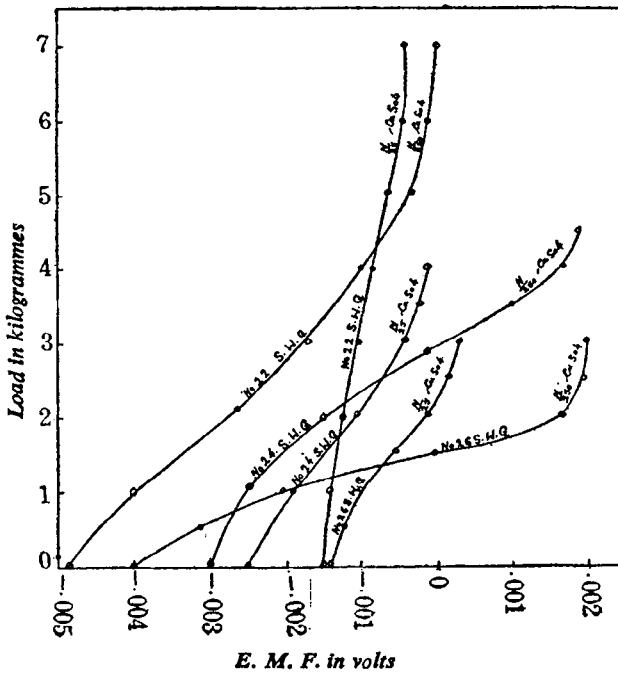


FIG. 2

resistance of the galvanometer was 450 ohms. The arrangement permitted the fall of potential of  $\cdot 00001$  volt being easily detected. The measurements were made by a potentiometric arrangement. The results of the experiments have been shown in the tables and graphs attached.

TABLE I

*The Copper Wire No. 22 S.W.G.  
in N/25 Copper Sulphate Solution*

Load applied (Kilogrammes)	E.M.F. Observed
0	$-\cdot 0015$ volt
1	$-\cdot 0014$
2	$-\cdot 0012$
3	$-\cdot 0010$
4	$-\cdot 0008$
5	$-\cdot 0006$
6	$-\cdot 0004$
7	$-\cdot 0004$

TABLE II

*The Copper Wire No. 24 S.W.G.  
in N/25  $\text{CuSO}_4$  Solution*

Load applied (Kilogrammes)	E.M.F. Observed
0	$-\cdot 0025$ volt
1	$-\cdot 0019$
2	$-\cdot 0010$
3	$-\cdot 0004$
3.5	$-\cdot 0002$
4	$-\cdot 0001$

TABLE III

*The Copper Wire No. 26 S.W.G.  
in N/25  $\text{CuSO}_4$  Solution*

Load applied (Kilogrammes)	E.M.F. Observed
0	$-\cdot 0014$ volt
0.5	$-\cdot 0012$
1	$-\cdot 0010$
1.5	$-\cdot 0005$
2	$-\cdot 0001$
2.5	$+\cdot 0002$
3	$+\cdot 0003$

TABLE IV

*The Copper Wire No. 22 S.W.G.  
in N/250  $\text{CuSO}_4$  Solution*

Load applied (Kilogrammes)	E.M.F. Observed
0	$-\cdot 0049$ volt
1	$-\cdot 0040$
2	$-\cdot 0025$
3	$-\cdot 0017$
4	$-\cdot 0010$
5	$-\cdot 0003$
6	$-\cdot 0001$
7	$\cdot 0000$

TABLE V

*The Copper Wire No. 24 S.W.G.  
in N/250  $\text{CuSO}_4$  Solution*

Load applied (Kilogrammes)	E.M.F. Observed
0	$-\cdot 003$ volt
1	$-\cdot 0025$
2	$-\cdot 0015$
3	$-\cdot 0002$
3.5	$+\cdot 0010$
4	$+\cdot 0017$
4.5	$+\cdot 0019$

TABLE VI

*The Copper Wire No. 26 S.W.G.  
in N/250  $\text{CuSO}_4$  Solution*

Load applied (Kilogrammes)	E.M.F. Observed
0	$-\cdot 0040$ volt
0.5	$-\cdot 0031$
1	$-\cdot 0020$
1.5	$0000$
2	$+\cdot 0017$
2.5	$+\cdot 0020$
2.75	$+\cdot 0020$

The constant term  $E_0$  in the Nernst expression  $E = E_0 + \frac{RT}{nF} \log c$  has been evaluated by Butler.<sup>2</sup> He puts the constant term  $E_0$  as being equal to  $\frac{W_1 - W_2}{nF} + \frac{RT}{nF} \log \frac{A N_s}{1000 N_1 A_1}$  where  $W_1$  is the work required to bring a positive ion from the metallic surface to the equilibrium point, similarly  $W_2$  represents the work required to bring a negative ion from the bulk of the solution to the equilibrium point,  $A_1 = V\sqrt{R/n} W_1$ ,  $A = \sqrt{R/2} \pi M$ ,  $M$  being the gram ion weight,  $N_1$  = number of ions per unit area of the metal surface,  $N_s$  = number of ions per c.c. of the salt solution. Other symbols having their usual meanings. Of the two terms occurring in the equation, the first term  $\frac{W_1 - W_2}{nF}$  is the only significant one and has a predominant value, the other terms according to Butler (*loc. cit.*) can be left out.

$W_1$  is the work done in bringing the metallic ion from the surface of the metal to the equilibrium point. Butler (*loc. cit.*) has not taken account of any resistance that would have to be overcome in detaching the metallic ion from the molecular aggregation.

The aggregates of crystals in the metals are of great complexity. When the metals are strained for instance as happens when they are stretched by a load, these aggregates which sometimes are as big as a fraction of a millimetre are altered. Ewing and Rosenhain<sup>3</sup> have made a special study of this fact and find that when a metal is strained beyond the yield point there is a slipping of the crystals as shown in Figs. 3 and 4.

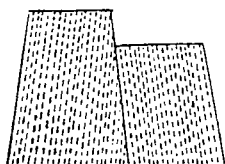


FIG. 3  
Before Straining

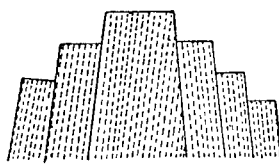


FIG. 4  
After Straining

The increase in the positive value of P.D. of the strained wire shows that the tendency for the copper to form ions under stretching strain becomes less as the weight is increased (Fig. 2) or that the molecular aggregates formed on the surface hinder the formation of ions. This means that the value of  $W_1$  in the case of strained wire is higher than in the case of annealed one.

It is also seen that when the strain is removed the P.D. against the annealed wire does not reach its original value showing that the

molecular aggregates and not the strain itself is responsible for the increase in the potential.

It is very difficult to keep wires free from any strain and therefore the curves have started from different E.M.F.'s although dipping in the same solution shown in Fig. 2.

It is also seen from the graph (Fig. 2) that after a certain load the P.D. becomes constant. This may be due to the fact that at this stage the wire approaches the breaking point and the deformation at the electrode surface is complete.

#### *Conclusion*

1. The potential differences of copper wires under stretching strain against annealed wires have been studied.
2. It is found that the strained wire is more positive.
3. It is contended that some work is necessary to detach ions from the metallic surface and is more in the case of strained wire as compared to the annealed one.

#### REFERENCES

1. Erlanger .. *Ber.*, 1934, **65**, 211-214.
2. J. A. V. Butler .. *Trans. Faraday Soc.*, 1924, **19**, Part III, p. 729.
3. Ewing and Rosenhain .. *Proc. Roy. Soc.*, **45**, p. 85.