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MEASUREMENT OF
STRESS POTENTIALS

by

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MEASUREMENT OF STRESS POTENTIALS.

I. INTRODUCTION.

The problem of corrosion prevention is of major importance in the highly mechanized industries of today. In order to be able to prevent or suppress corrosion, it is necessary to know what causes the formation of the corrosion product. It has been well established that the process of corrosion is electrochemical.¹ Consequently, we may say that a difference of potential must exist between two or more parts of the system under consideration. The problem, then, becomes one of finding the cause of these potential differences.

The potential difference associated with a free energy change may be calculated by using the equation

¹ Warner, J. C., Trans. Am. Electrochem. Soc. Vol. 83 pp 319-333 (1943)

$$-\Delta F = n f E$$

where $-\Delta F$ = the free energy change in calories

n = valance change produced

f = the faraday (23,070 cal./volt)

E = the potential difference of the corrosion couple in volts.

Also, the increase of free energy is a measure of the net work done.² Therefore, if work is done on part of a system, it should develop a corresponding change in potential. A potential difference will result between the part that has suffered the free energy change and other, unaffected parts of the system; and in the presence of an electrolyte, corrosion products will form.

An important practical case is corrosion caused by strains in metals. These may be produced by either internal stresses or external applied stresses. A potential difference is set up between the strained and unstrained parts, and where these occur on an exposed surface, a corrosion couple may result. The importance of proper annealing and heat treatment to remove internal strains has received considerable attention. 3, 4, 5.

2 Glasstone, S., Textbook of Physical Chemistry, New York, Van Nostrand, 1940, p. 224.

3 Heheman, R. F. et al., Metals and Alloys, Vol. 19 pp. 1141-4 (1944)

4 Günter Wasserman, Z. Mettalkunde, Vol. 35, pp 79-84, (1943)

5 Waber, J.T. et al., Trans. Am. Electrochem., Soc. Vol. 87, 23pp. (Preprint(1945)

These workers have shown that there is a definite relationship between aging, annealing etc., and the rate of corrosion. However, little work has been done to establish the rate of corrosion by considering the basic cause, namely, the size of the potential difference produced between the strained and unstrained parts. W. Walker and C. Dill⁶ determined the effect of stress upon the electromotive force of iron. Earlier work had been done on the determination of the potential difference between pairs of steel rods, one of which had been strained beyond its elastic limit.⁷

However there appears to be no work done on the determination of the steady state potential differences produced by varying the stress applied to a part of a metallic system. The work represented by this thesis attempts to find a relationship between the difference in applied tension between two wires of the same metal suspended in an electrolyte, and the potential difference that is produced. Hereafter the potential difference resulting from applied stresses will also be referred to as the "stress potential."

⁶ Walker and Dill, Trans. Am. Electrochem., Soc., Vol. 11, pp 153-168 (1907)

⁷ Andrews, T., Proc. Inst. Civil Eng. (British) 118-356 (1894)

II THEORY.

The change in potential that one would expect to be produced may be computed on the assumption that the energy stored in the specimen is available as potential energy.⁸ Consider the work done on a unit centimeter cube of the metal when it is strained by any given amount up to the elastic limit:

$$W = \frac{1}{10^7} \int_0^T f dl$$

where W = work done in joules

f = stress applied in dynes

l = strain produced in centimeters

Since $\frac{f}{l} = Y$ = modulus of elasticity

$$dl = \frac{1}{Y} df$$

Substituting the original equation,

$$W = \frac{1}{10^7 Y} \int_0^T f df$$

Integrating,

$$W = \frac{1}{10^7 Y} \frac{T^2 - 0}{2} = \frac{T^2 10^{-7}}{2Y} \text{ joules.}$$

Where T = tension applied in dynes/cm²

Y = modulus of elasticity.

⁸ Walker and Dill, op cit., pp. 157-8

Now a unit centimeter cube of metal contains $\frac{n\rho}{A}$ equivalents, where

A = Atomic weight

n = valence change produced

ρ = density of metal in gm/cm³

Therefore the work done in joules per equivalent is

$$W/\text{equiv.} = \frac{T^2 10^{-7}}{2Y} \cdot \frac{A}{n\rho}$$

To convert to volts:

$$\text{Volts} = \frac{\text{joules}}{\text{coulomb}} = \frac{\text{joules/equiv.}}{\text{coulombs/equiv.}}$$

but coulombs per equivalent = the Faraday = 96500

Therefore,

$$\text{Volts} = \frac{T^2 10^{-7} A}{2Yn \cdot 96500} = \frac{T^2 A 10^{-12}}{1.93 Yn\rho}$$

As an example, consider the potential produced in a length of 24 gauge, cold drawn copper wire under a stress of one kilogram. Area of 24 gauge wire (British Standard Gauge) is 0.00245cm².

Therefore

$$T = \frac{1000(980)}{0.00245} = 4 \times 10^8 \text{ dynes/cm}^2$$

For cold drawn copper wire, $Y = 11 \times 10^{11} \text{ dynes/cm}^2$

Also, $A = 63.57$, $\rho = 8.92$ and for reasons that will be given later, n is chosen as 2.

$$\begin{aligned} E &= \frac{(4 \times 10^8)^2 (63.57) 10^{-12}}{1.93 (11 \times 10^{11}) 2 (8.92)} \\ &= 2.46 \times 10^{-7} \text{ volts.} \end{aligned}$$

At first glance it would appear that the strained wire will be positive to an unstrained wire, that is, the unstrained wire will go into solution. But consider the solution pressure of the metal—the basic factor that establishes the direction of the current of electrons. When the stress is applied, the crystal lattice of the wire suffers a deformation and therefore a weakening in the lattice bonds. One could logically conclude that there should be an increase in the solution pressure because of the weakened bonds. Thus the strained wire is the negative pole and will go into solution. This conclusion was proven correct by the experimental results.

In the case of copper, it appears that the metal goes into solution with a loss of two electrons. There is no proof for this other than the fact that experimental results, especially for annealed copper, justify this assumption (see Fig. 4.,).

III. APPARATUS AND PROCEDURE.

The basic requirements for an apparatus to measure stress potentials were, first, a cell, containing the electrolyte in which the stressed and unstressed wires could be suspended; and second, a device to measure the potential difference between the wires.

To ensure that no ~~other~~ potentials would be present other than that set up in the stressed wire, it was necessary to exclude all other metal from the cell. Figure I shows the cell in its final form.

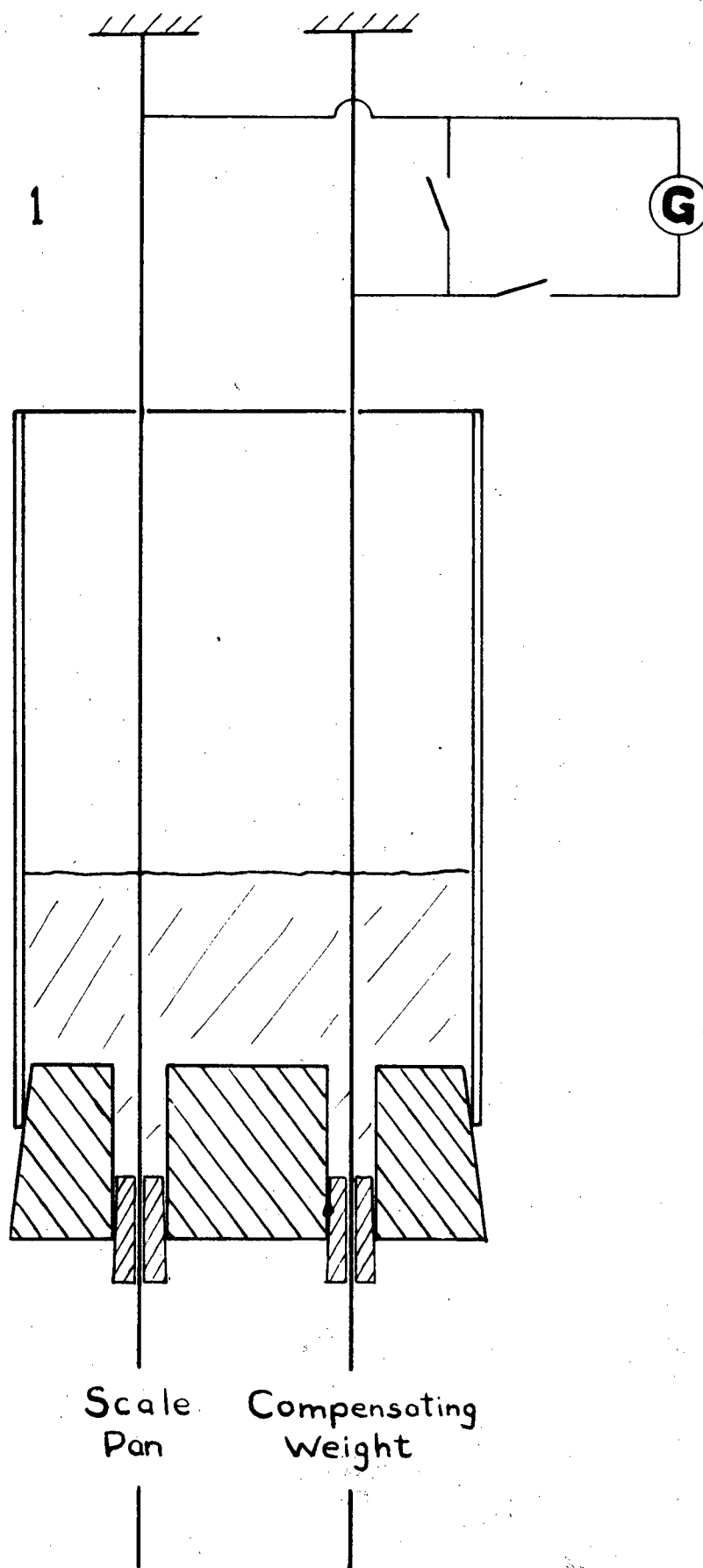
(a) The Test Cell.

The main body consisted of a 15 centimeters length of 80 millimeter pyrex glass tubing closed at the bottom with a rubber stopper. Two 15 millimeter holes were drilled through the rubber stopper, about three centimeters apart. These holes had to be plugged in such a way as to allow the wires to hang freely through them, but to prevent the electrolyte from running out. The following device proved excellent for such a purpose:

The centres of two single-hole rubber stoppers were drilled out from the smaller end, to a depth of about one centimeter. Into these holes were forced 5 millimeter lengths of capillary tubing, having a bore slightly larger than the diameter of the wire being tested. The space above the capillary tubing was then packed with stop-cock grease. Figure II gives a detailed cross-section view of the resulting water-tight plug, which permitted the wire to slide through freely under any imposed stress, but prevented the electrolyte from leaking out of the cell.

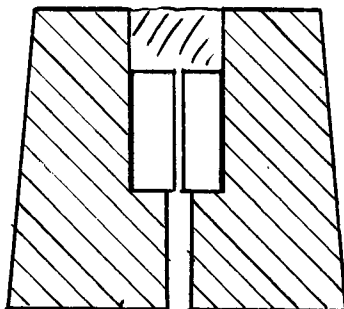
The wires to be tested were suspended from well-

FIGURE 1



insulated hooks that hung from the ceiling. A 200 gram scale pan was hung from the lower end of the wire to be placed under stress, and a 200 gram weight was suspended from the other wire to counterbalance any effect due to the scale pan. This weight was found to be sufficient to remove any curl in the wires and keep them hanging vertically.

Figure II



(b) Measurement of Stress Potential.

A type "K" potentiometer, capable of measuring 10^{-7} volts was first used to measure the potential difference but proved unsatisfactory, and had to be replaced by a simple suspension mirror galvanometer of known sensitivity. The potentiometer was the obvious choice to make the voltage measurement, and it was the device used by

⁹
Walker and Dill in their experiments on soft iron. However, when it was found that the stress potential was upset to such an extent that the reading drifted constantly, the assumption was made that the potentiometer counter-voltage was at fault. A suspended-mirror galvanometer of 150 ohms resistance and a sensitivity of 0.05 microvolts per millimeter was substituted. The change was very fortuitous, because it was now found that not only had the potentiometer upset the stress potentials, but it had in some manner created a potential difference between the wires that did not exist. Whereas the potentiometer had indicated differences in potential as high as twenty millivolts between the wires that were under equal tension, the galvanometer indicated potential differences of the order of a few microvolts.

The galvanometer leads were attached to the wires in the test cell by a collar-and-screw arrangement that gave good electrical contact. Soldering the leads on may have given slightly better contact, but the heat necessary for soldering would have weakened the wires structurally by annealing them to some extent. Heavy copper wire was used in all leads to keep the resistance down to a minimum. A knife-edge switch was inserted in the line, and another was attached across the leads as a protective short for the galvanometer. The leads and

points of contact had only a fraction of an ohm resistance, so that the voltage drop across the galvanometer^e was essentially the same as the potential difference between the wires being tested.

Tests were made primarily on copper wires, both annealed and cold-drawn; and also on cold-drawn brass and platinum wires.

The main electrolyte used was four per cent solution of NaCl. Solutions of Na_2CO_3 , Na_2SO_4 , CuCl_2 , NH_4Cl , and KCl, were also used to determine what effect, if any, the electrolyte had on the potential differences produced. All solutions were made with distilled water that was re-boiled immediately prior to its use in order to remove all dissolved gases.

A cathetometer, capable of measuring to 0.005 centimeters, was used to determine whether the wires were strained permanently and also to check approximately the elastic limits of the wires.

(c) Method of Testing.

Approximately three-foot lengths of the wire to be tested were first thoroughly cleaned with ether to remove grease and dirt. Harsher treatment, such as washing with acid was deemed inadvisable because of the possibility of inducing the formation of an oxide layer on the metal surface.

Since stressing a wire would bring a fresh section into the electrolyte at the top and remove a part at the bottom, it was found expedient to cover both wires with a waterproof coating, leaving exposed a measured amount that was certain to stay in solution during the test. The best results were obtained by using melted paraffin wax to coat the wires. On hardening, the wax adhered very well to the wire and was sufficiently elastic to stretch with the wire when the latter was under stress.

After receiving their coating of wax, the wires were strung through the water-tight plugs and the galvanometer leads were attached. Sufficient electrolyte was poured into the cell to cover the exposed portions of the wires, and the galvanometer switch closed. As a precaution against momentary, relatively high, voltages that appeared on the instant of completing the circuit, the galvanometer shorting switch was always closed for the first few minutes. Once the voltage had died down sufficiently, the shorting switch could be opened, and the voltage could then settle to a constant reading. Once the voltage became constant, the scale pan on the test wire could be loaded and the corresponding change in potential difference read off the galvanometer scale. Frequently, it was necessary to let the wires remain in the solution for several

hours before the potential difference would die down sufficiently to permit the use of the galvanometer.

The galvanometer scale extended for 25 centimeters on both sides of zero deflection, and could therefore measure potential differences up to 12.5 microvolts.

IV. EXPERIMENTAL RESULTS.

It was found that all pairs of wires even before tension was applied, exhibited a certain inherent amount of potential difference. This varied from about one to ten or more microvolts, with either wire being the more positive. No two wires were ever found that gave zero potential difference. In fact some lengths of wire could not be tested because the inherent potential difference was great enough to send the galvanometer deflection off the scale, even after several days of shorting. Usually, putting in a fresh length for either or both wires would give a potential difference small enough to be read on the galvanometer scale. The need for the wax coating was also quickly proven, because if the wires were not coated as previously described, the addition of a fraction of a centimeter of electrolyte would cause a change in the potential difference amounting to several microvolts.

(a) Variables.

From the theoretical equation derived, the only

variable to affect the potential difference produced by a pair of wires of any one metal is the force that is applied per unit area (assuming isothermal conditions throughout). However, it does not seem unreasonable to suspect that other factors may influence the potential produced, namely:

1. Length of wire in electrolyte.
2. The electrolyte used.
3. The concentration of the electrolyte.

Tests were made to ascertain the presence or absence of the influence of these three variables.

To test for the effect of length of wire in solution, 24 gauge cold drawn copper wire (diameter = 0.0559cm) and a four percent solution of NaCl were used. For the first test, a one-centimeter length of each wire was left bare in the electrolyte. A stress of one kilogram (408.2Kg/cm^2) was applied and the corresponding change in potential difference was found to be 2.5×10^{-7} volts. One wire was then replaced by another having two centimeters bare and the test repeated. The length of bare wire was increased in increments of one centimeter until one wire was bare for a length of ten centimeters in the solution. The other was similarly changed in steps of one centimeter, up to a bare length of ten centimeters. The change of potential difference on the application of a one kilogram stress was measured for each step. A few of the

results are given in Table I.

Table I.

Variation of Stress Potential with Length of Wire
in Electrolyte.

Length of bare wire - centimeters.		Potential Difference.
Stressed Wire	Unstressed Wire	-volts-
1	1	2.5×10^{-7}
5	1	2.25×10^{-7}
10	1	2.25×10^{-7}
10	5	2.75×10^{-7}
10	10	2.0×10^{-7}

The results show conclusively, within experimental error, that the potential difference produced is independent of the length of wires in the solution. However, it was found that the more wire that was exposed to the solution, the unsteadier was the potential difference, that existed between the unstrained lengths of wire, sometimes preventing tests because of a constant drift in the reading. Consequently, in order to be sure of a steady voltage at the start of a run, it was found desirable to leave only a fraction of a centimeter of each wire exposed to the solution.

The choice of NaCl solution as the electrolyte was made because of its widespread appearance as salt water and consequent importance as a factor in corrosion.

However, it was necessary to try other electrolytes as a check on whether the potential difference produced was independent of the electrolyte or not.

Tests with other electrolytes were made in the following manner:

The cell was assembled. using 24 gauge cold drawn copper wires, and NaCl solution added. One wire was then stressed with one kilogram (408.2 Kg/cm^2) and the change in potential difference recorded. The NaCl solution was then washed out without disturbing the wires and a different electrolyte added. The change of potential difference caused by one kilogram was again noted. As a check, the electrolyte was removed, NaCl solution again poured in, and the wire once more stressed with one kilogram. If the repeat test with NaCl did not give a stress potential reasonably close to the first test, the test was discarded. The results obtained for the various electrolytes are summarized in Table II (all solutions were 4%).

Table II.Variation of Stress Potential with Electrolyte Used.

Electrolyte.	P.D. produced by one kilogram stress -volts.
NaCl	2.5×10^{-7}
Na ₂ SO ₄	no deflection
KCl	2.5×10^{-7}
Na ₂ CO ₃	no deflection
CuCl ₂	(off scale)
NH ₄ Cl	(off scale)
NaCl plus 1cc HCl	(off scale)
NaCl plus 1cc NaOH	(off scale)

We can conclude from these results that the last four solutions probably produced a chemical potential by attacking the wires. This potential was much larger than that inherent in the wires and in all trials was found to produce a deflection far off the scale, even after prolonged shorting of the two wires.

The cases of Na₂SO₄ and Na₂CO₃ are also very interesting. For both electrolytes the initial potential difference between the wires was much lower than that usually obtained when using NaCl; but the chief point of interest was that in neither case did any stress potential develop when the wire was stressed, and the stress increased beyond the elastic limit. A slight deflection was noted at the instant of application of the stress

but it immediately died down. For Na_2CO_3 this behaviour can easily be explained by the fact that CuCO_3 is very insoluble and may form as a protective coating on the wires. Once this is formed on the surface of the wires, applying a stress will not produce a stress potential. Any potential difference present is probably due to dissimilarity in the precipitated coatings and remains constant even though the wire is being stressed. Any slight deflection would be due to a temporary break in the CuCO_3 coating on the stressed wire, caused by the change in strain on the instant of application of more weight.

However, CuSO_4 is quite soluble so that a similar explanation does not hold for Na_2SO_4 . It may be that the copper develops some sort of passivity in this electrolyte which prevents a free transference of electrons at the metal surface.

For all subsequent tests, NaCl was used, but first the effect of concentration on the stress potential had to be determined. A series of tests were made on NaCl at various concentrations, using 24 gauge cold drawn copper wire and the results are given in Table III.

Table III.Variation of Stress Potential with Concentration of Electrolyte

Concentration of NaCl	P.D. produced by one Kg stress - volts.
2%	2.25×10^{-7}
4%	2.0×10^{-7}
8%	2.25×10^{-7}
16%	2.0×10^{-7}

These show conclusively that the stress potential is independent of the concentration of the electrolyte.

All subsequent tests were done using a 4% NaCl solution.

(b) Copper Wire Tests.

Tests were made on both annealed and cold drawn copper wire. Wires of three gauges were used, namely: 18 gauge (0.1219 centimeter diameter), 21 gauge (0.0813 centimeters diameter), and 24 gauge (0.0559 centimeters diameter). The cross-sectional areas of these three gauges differ approximately by factors of two. Use of these gauges quickly established the fact that the potential difference due to stress depended on the stress per unit area. Thus, for a given applied stress, the voltage obtained from a 24 gauge wire was approximately double that obtained from a 21 gauge wire and four times that given by an 18 gauge wire. A sample run for 24 gauge cold drawn copper wire in 4% NaCl solution is shown in

Table IV. Generally at least two minutes were required to give a constant reading, because immediately after application of stress there was a momentary deflection corresponding to several microvolts. However, this died down quite rapidly to give a constant reading.

Note in Table IV that the stress potential rises linearly with the stress applied up to a point between 2450 and 2850 kg/cm², then drops off. Compare this to the accepted value of 2671.5 kg/cm² for the elastic limit of cold drawn copper wire. It would appear that when the metal is stressed beyond its elastic limit, that is, develops a permanent set, the crystal lattice structure is ruptured to some extent so that there is no further increase in the solution pressure and consequent increase in the stress potential. On the other hand, the damaged lattice develops a permanent stress potential that is only slightly smaller than the maximum recorded.

The two sudden changes in the potential difference that occurred at 2:38 and 2:50 are quite inexplicable. Most runs had one or two such changes for no apparent reason. They did not affect results in any way.

The "L" in the scale reading column denotes a deflection to the left. This implies that of the two wires, the stressed wire was inherently more negative than the unstressed one. Adding the stress would then increase the potential difference. In other runs, the

Table IV.

Variation of Stress Potential with Applied Stress for
Cold Drawn Copper Wire.

Time	Stress Kg.	Scale Reading cm.	Potential Diff- erence -volts	Stress Potential volts	Unit Stress Kg/cm ²
2:15	0	22.2 L	111.0×10^{-7}	0	0
2:17	4	22.7 L	113.5×10^{-7}	2.5×10^{-7}	408.2
2:20	0	22.2 L	111.0×10^{-7}	0	0
2:23	2	23.2 L	116.0×10^{-7}	5.0×10^{-7}	816.4
2:25	0	22.2 L	111.0×10^{-7}	0	0
2:30	3	23.7 L	118.5×10^{-7}	7.5×10^{-7}	1224.6
2:32	0	22.2 L	111.0×10^{-7}	0	0
2:38	0	14.0 L	70.0×10^{-7}	0	0
2:40	4	16.0 L	80.0×10^{-7}	10.0×10^{-7}	1632.8
2:42	0	14.0 L	70.0×10^{-7}	0	0
2:47	5	16.5 L	82.5×10^{-7}	12.5×10^{-7}	2041.0
2:50	0	15.7 L	78.5×10^{-7}	0	0
2:54	6	18.6 L	93.0×10^{-7}	14.5×10^{-7}	2449.2
3:00	0	15.7 L	78.5×10^{-7}	0	0
3:04	7	18.5 L	92.5×10^{-7}	14.0×10^{-7}	2857.4
3:10	0	18.0 L	90.0×10^{-7}	11.5×10^{-7}	0

the unstressed wire was originally more negative, and an application of stress would lower the potential difference.

(c) Results.

Graph I shows the variation of stress potential produced with the stress per unit area applied for cold drawn copper wire.

Graph II shows the variations of stress potential with stress per unit area for annealed copper wire. The curve drawn in as a dotted line represents the theoretical variation as obtained by using the formula on page 5, taking "n", the valence change as equal to two. This type of wire was the only one to follow the theoretical curve fairly closely. All others tested gave definitely linear results except when past the elastic limit, where the stress potential either dropped or levelled off.

Some samples of 36 gauge platinum (diameter $\neq 0.02\text{cm}$) wire were also tested. However it was found that platinum is completely passive, even when stressed to the breaking point. The original (inherent) potential difference of the two wires never gave a deflection of more than a fraction of a millimeter off the zero point. Loading one wire never gave more than a millimeter or ~~two~~ momentary deflection. Compare this to copper or brass which gave momentary deflections of ten to one hundred

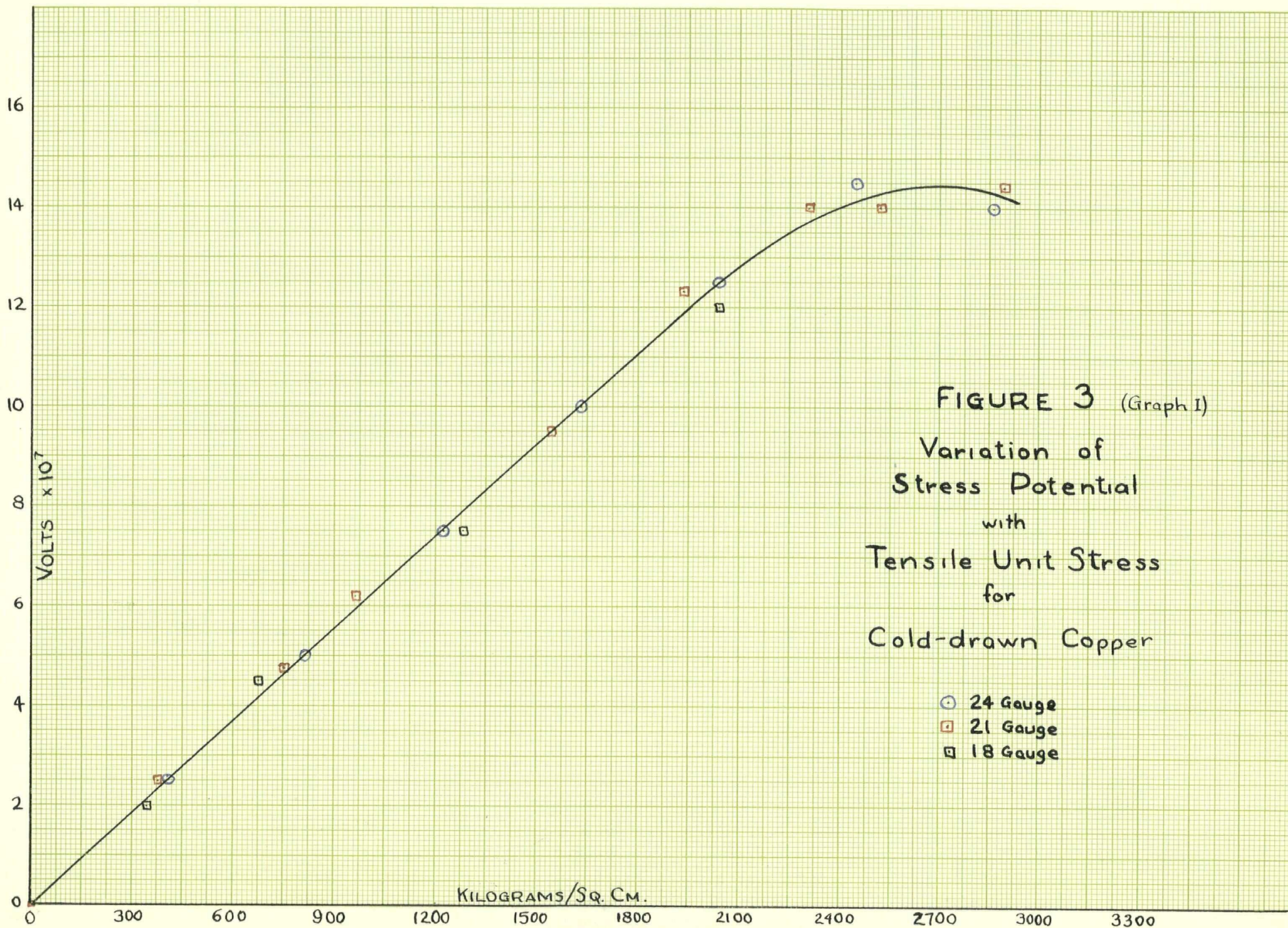
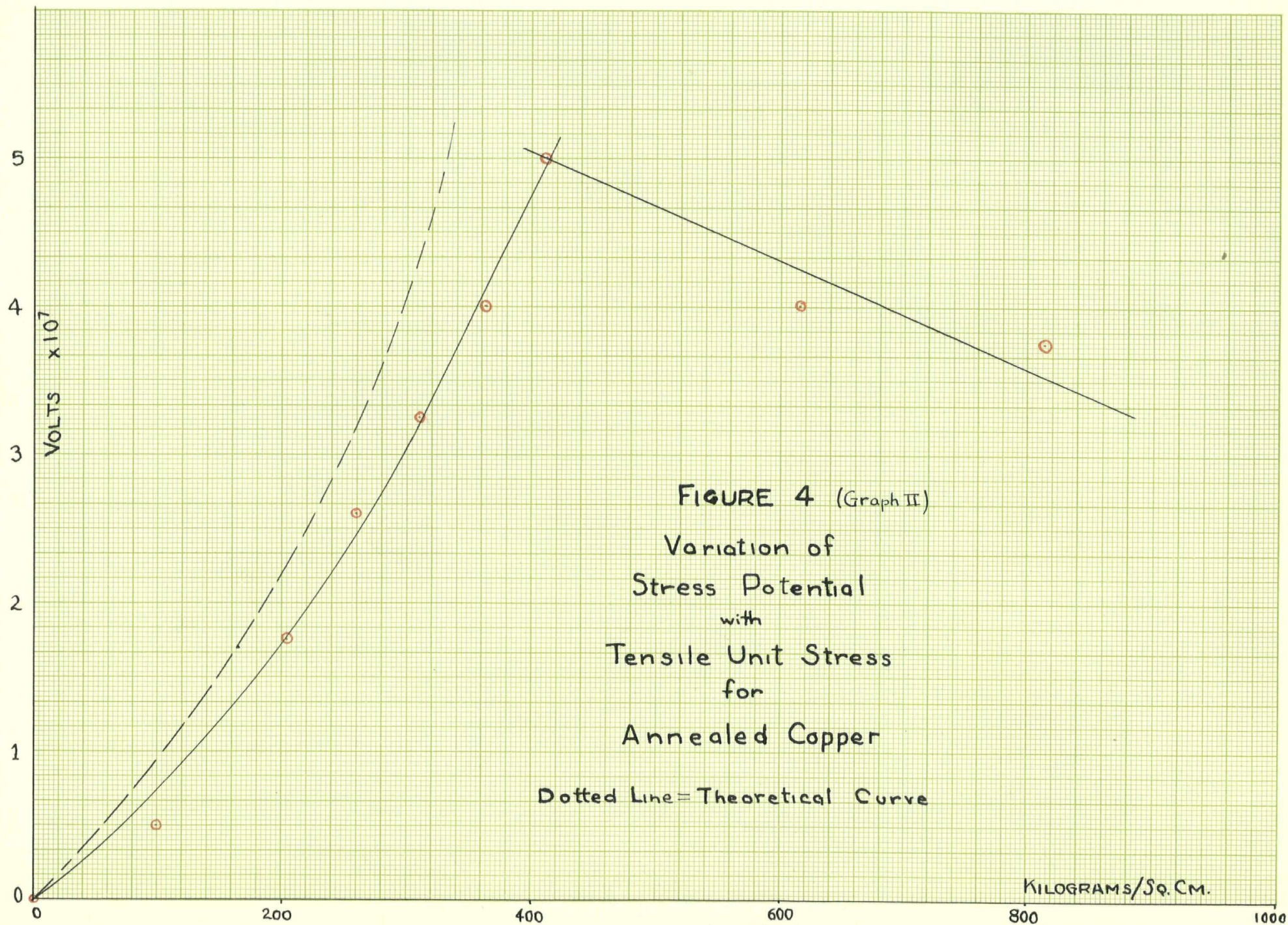


FIGURE 3 (Graph I)
Variation of
Stress Potential
with
Tensile Unit Stress
for
Cold-drawn Copper

- 24 Gauge
- 21 Gauge
- 18 Gauge



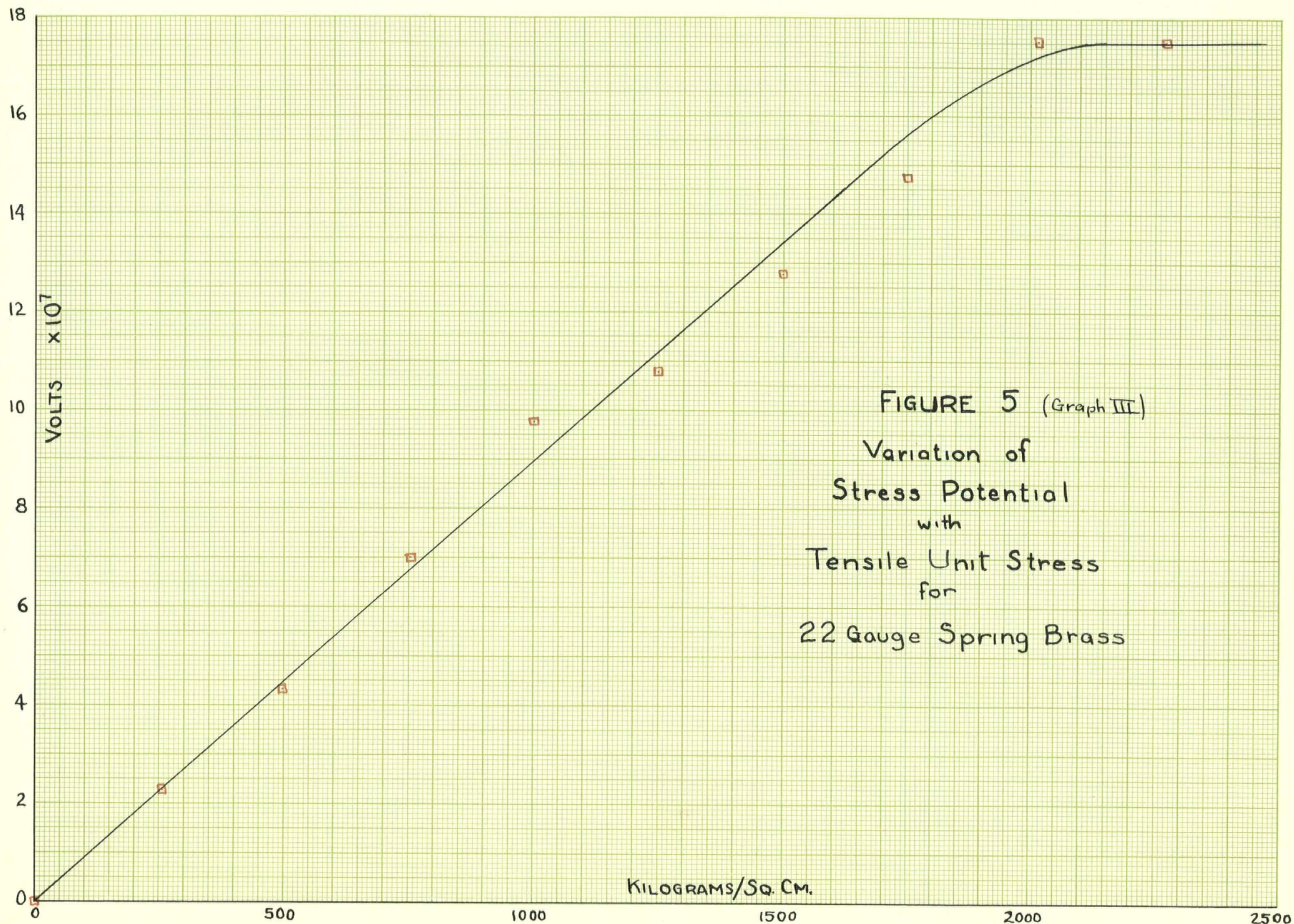


FIGURE 5 (Graph III)
Variation of
Stress Potential
with
Tensile Unit Stress
for
22 Gauge Spring Brass

times as much. This is not unexpected, since platinum is very low in the electromotive series, and does not oxidize easily.

Graph III shows the variation of stress potential with stress per unit area for 22 gauge (diameter = 0.0711cm) spring brass wire.

The behaviour of the stress potential could not be investigated much beyond the elastic limit in most cases because the wires broke, usually at the point where they were attached to the ceiling hooks.

V. CONCLUSION.

It may be concluded that in the presence of some electrolytes, a potential difference is developed when a strain is produced by either internal or applied external stresses in a part of the system under consideration. If the corrosion product of a stress potential cell is insoluble, the potential due to the stress is negligible.

All results obtained were easily reproducible with only slight variations between the different samples of wire.

It is interesting to note that the stress potential curves for both cold drawn copper and brass behave exactly as their stress-strain curves do. That is, there is a linear relationship up to the elastic limit, after

which point the curve levels off irregularly. This is quite the opposite to what Walker and Dill reported in their work ¹⁰. However since they used a potentiometer to measure the potential difference produced, it may be that the potentials they obtained were being created and sustained in a manner similar to that described on page 10 of this thesis.

Should any further work be done on stress potentials there is one further suggestion that can be made. There must be no electrical equipment such as motors, etc., in the vicinity of the test cell. It was found that a one-eighth horsepower electric motor, operating at a distance of fifteen feet from the cell, was sufficient to produce a continuous oscillatory drift in the galvanometer reading over a range of several centimeters.

10 Walker and Dill, Trans. Am. Electrochem. Soc., Vol. ii, p. 167 (1907).

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