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THE
MECHANISM OF SOLID VISCOSITY

BY

CARL BARUS

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DEPARTMENT OF THE INTERIOR,
U. S. GEOLOGICAL SURVEY,
DIVISION OF CHEMISTRY,
Washington, D. C., August 31, 1891.

SIR: I transmit herewith a manuscript by Dr. Carl Barus entitled "The Mechanism of Solid Viscosity," with the request that it be published as a bulletin of the Survey. It represents work done in the physical laboratory.

Very respectfully,

F. W. CLARKE,
Chief Chemist.

Hon. J. W. POWELL,
Director.

PREFACE.

In the following pages I have brought together such of my experiments on the viscosity of solids as have an immediate bearing on the molecular mechanism by which viscous motion in solids is promoted. The bulletin is therefore a continuation of the previous publication (Bulletin 73), in which the phenomenon of viscosity was considered more particularly with reference to its physical manifestations. Most of the chapters of the present work are short, and a preliminary survey of the work done can be expeditiously made by consulting the table of contents.

C. B.

THE MECHANISM OF SOLID VISCOSITY.

By Carl Barus.

CHAPTER I.

TENSILE, DRAWN, AND OTHER STRAINS IN THEIR BEARING ON MAXWELL'S THEORY OF VISCOSITY.

INTRODUCTORY.

1. It is known that the effect of drawing metallic wires through a draw-plate is a marked decrease of the viscosity of the originally soft metal. The diminution increases with the intensity of strain imparted. It is not so well known that the viscous effect of a tensile strain applied in any degree to the same originally soft metal is after straining almost *nil* in comparison. Kohlrausch[1] and his pupils, Streintz[2] and others, more recently and in extensive researches Mr. Herbert Tomlinson,[3] have occupied themselves with these phenomena. The results of these observers are in general accord, and agree well enough with my work that special publication of new data might appear superfluous. Nevertheless, as steel has been but sparingly dealt with, and as results fitting at once into my diagrams are essential to my purpose, I have found it desirable to communicate them. Apart from these considerations the observations which I need must be made with minute reference to Maxwell's theory. In this respect the earlier work is seriously lacking.

The striking difference in the permanent viscous effect produced by the action of the two strains is particularly surprising, because the strains are imparted by mechanical processes not altogether dissimilar. The action of wire-pulling, however, accompanied as it is by surface compression as well as longitudinal extension, is conducive to the permanent retention of high-strain intensities, because it imparts to the wire an arched structure. In steel, at least, there is a dense shell surrounding an unusually rare core in such a way that the density of the

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[1] Kohlrausch's original and fundamental researches are given in my earlier papers. Here I need refer only to Schroeder, Wied. Ann., vol. 28, 1886, p. 354.

[2] Streintz, Pogg. Ann., vol. 153, 1874, pp. 395, 396, 411.

[3] H. Tomlinson, Phil. Trans., 1886, vol. 2, pp. 801 to 837. The variety of strains and metals examined in this paper give it unique value as regards the subject of the present section.

whole mass is materially lessened.[1] Conditions favorable to the retention of high-strain intensities are also conditions favorable to the occurrence of molecular instability. Hence the marked loss of viscosity of a drawn wire, as compared, cæt. par., with a soft wire. This premised, it appears that in the case of a wire hardened by simple traction the strain retained after traction is of insufficient intensity to be accompanied by marked molecular instability. More rigorously: if the wire during traction has experienced a strain S, which strain after the tensile stress is withdrawn diminishes to S′ ($S > S'$), then the wire need exhibit no change of viscous quality. For in the above cases of thermal annealing and torsional motional annealing (§§ 2, 9), the greater tensile strain S, supposing its action sufficiently prolonged, has wiped out all motional instability for strains $S' < S$; so it follows here that to evoke viscous deformation by aid of tensile strains, the wire must be examined *during traction*, and preferably under conditions of strain near the limit of rupture.

APPARATUS.

2. The apparatus used in these experiments is shown in Fig. 1, in which *ab* and *cd* are the two steel wires to be counter-twisted. The system is fastened above and below to two massive torsion-circles, A and B, respectively. The inner ends of the wires are joined by a strong brass rod *bc*, carrying a symmetrical circular platform near the lower end, on which the lead scale-weights C C′ C″, etc. (4 kilos. to 5 kilos. each) may be supported. In order to facilitate quick work, the connecting rod *bc* is provided with a pair of cross-vanes, D, D′, submerged in the water contained in an annular trough, *fgih f′g′i′h′*. Finally, the mirror *m* adjustably attached to the rod *bc* (readings by telescope and scale) indicates the difference of viscous motion of the two wires in consequence of a fixed rate of twist stored between A and B. I may add that the rod *bc* can easily be chosen light enough, compatibly with strength, to introduce no viscous effect of its own.

DATA FOR DRAWN WIRES.

3. The data to test the above are given in the following tables, of which Nos. 1, 2, 3 exhibit the behavior of some drawn steel wires. In each case the comparison is made with my steel normal No. 15 (the lower wire in Fig. 1, An. 450° and twisted to permanent viscous qualities). The drawn wire in Table 1 is in the moderately resilient bright commercial state, very soft to the file. The wire in Table 2 has been drawn down from a larger diameter and the same state of hardness to an extreme of brittle resilience. The wire of Table 3 finally was first softened by heating to redness in air and then drawn down to brittle resilience. Dimensions are given in the tables, ρ being the radius and l

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[1] Cf. Baumeister: Dissert., Würzburg, 1883.

and l' the lengths of the wires. $L = l + l'$. The impressed rate of twist in radians is given under τ. The observed permanent torsion is $2(\varphi + \varphi')$. θ and θ' are the temperatures of the drawn and normal wires respectively. The former is constant, the latter (θ') at first 30°, and then 100°; so that the examination is made at two temperatures, in order to compare corresponding viscous effects of the drawn strain and of temper. As will be more fully shown below, § 5, $\tau + 2(\varphi + \varphi' (= 2\pi/L$, and $(\varphi - \varphi')/\tau$ is the viscous deformation indicated by the mirror, per unit of length of system, per unit of τ. It must be borne in mind (cf. § 13) that $(\varphi - \varphi')/\tau$ is a function of τ, for which reason the same rate of twist is applied to the wires throughout; applied, moreover, positively and negatively for each value of θ'. Finally, after testing the wire in the drawn state, it was softened by heating to redness in air and again tested. In this case viscous motion at the mirror nearly ceases, thus affording an excellent check on the validity of the experiments.

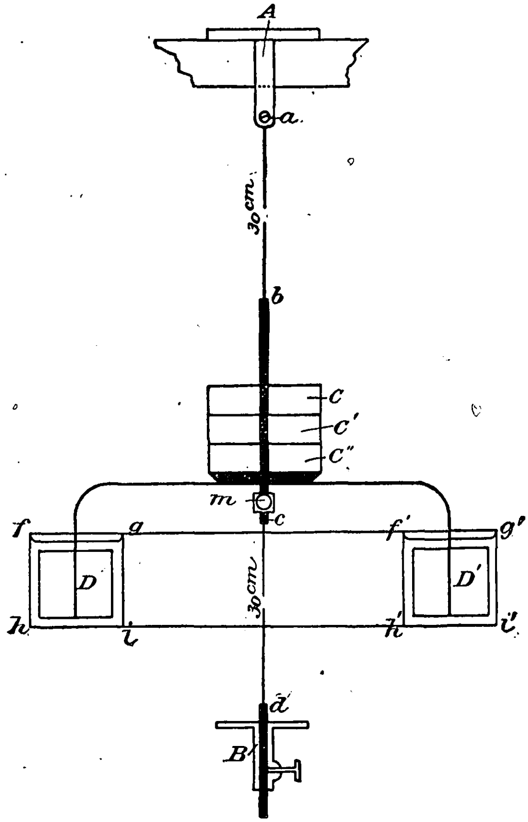

Fig. 1.—Apparatus for comparing viscous deformations.

TABLE 1.—*Viscosity of hard-drawn steel wire compared with soft.*

$2\rho = {\cdot}082$ cm.; $L = l + l' = 30$ cm. + 30 cm.

Wire drawn moderately resilient.				Same wire annealed at red heat in air.			
θ θ'	τ $2(\phi+\phi')$	Time.	$\frac{\phi-\phi'}{\tau}\times 10^3$	θ θ'	τ $2(\phi+\phi')$	Time.	$\frac{\phi-\phi'}{\tau}\times 10^3$
		h. m.				*h. m.*	
30	+ ·1041	1 36		30	+ ·1034	3 08	
30		38	·00	30		10	+ ·00
		39	1·08			11	·10
		44	3·33			13	·07
	+ ·0037	48	4·43			16	·10
					+ ·0014	20	·14
30	— ·0989	1 51		30	— ·1019	3 22	
30		53	— ·00	30		24	+ ·00
		54	—1·01			25	·00
		56	—2·35			27	·03
		59	—3·58			30	·07
	— ·0058	63	—4·61		— ·0028	34	·07
100	+ ·0989	2 24		100	+ ·1047	4 00	
30		26	·00	30		02	·00
		27	2·83			03	·33
		29	6·53			05	·78
		32	10·23			08	1·31
	+ ·0058	36	13·60		+ ·0000	12	1·44
100	— ·0931	2 39		100	— ·1004	4 13	
30		41	·00	30		15	— ·00
		42	3·03			16	— ·33
		44	7·07			18	— ·88
	— ·0116	47	10·77		— ·0043	21	1·65

TABLE 2.—*Viscosity of hard-drawn steel wire compared with soft.*

$2\rho = {\cdot}082$ cm.; $L = l + l' = 30$ cm. $+ 30$ cm.

Wire drawn ($2\rho = {\cdot}13$ cm. to ${\cdot}08$ cm.) very resilient.				Same wire annealed at red heat in air.			
θ θ'	$\frac{\tau}{2(\phi+\phi')}$	Time.	$\frac{\phi-\phi'}{\tau} \times 10^3$	θ θ'	$\frac{\tau}{2(\phi+\phi')}$	Time.	$\frac{\phi-\phi'}{\tau} \times 10^3$
		h. m.				*h. m.*	
30	+·0959	5 52		30	—·1019	1 32	
30		54	·00	30		34	
		55	4·37			35	—·00
		57	10·10			37	—·13
		60	15·68			40	—·17
		63	19·46		—·0028	44	—·20
	+·0087	6 30	34·47				
30	—·0916	6 32		30	+·1034	1 45	
30		34	— ·00	30		47	+·00
		35	— 4·72			48	·10
		37	—10·50			50	·10
		40	—16·16			53	·15
	—·0131	44	—20·88		+·0014	57	·21
100	+·0916	6 52		100	—·1019	2 00	
30		53	·00	30		02	— ·00
		54	16·80			03	— ·47
		55	27·30			05	— ·91
		56	34·50			08	—1·28
	+·0131	56·7	39·05		—·0028	12	
100	—·0873	6 58			Accident.		
30		59	— ·00				
		60	—16·80				
		61	—26·30				
		62	—33·70				
	—·0175	63	—39·40				

TABLE 3.—*Viscosity of hard-drawn steel wire compared with soft.*

$2\rho = {\cdot}082$; $l = l' =$ cm.; $\theta = \theta'$ 30°. Wire drawn ($2\rho = {\cdot}13$ to $\cdot 08$ cm.) very resilient.

$\overset{\tau}{(2\phi+\phi')}$	Time.	$10^3 \times (\phi - \phi')/\tau$	$\overset{\tau}{2(\phi+\phi')}$	Time.	$10^3 \times (\phi - \phi)/\tau$
	h. m.			*h. m.*	
+ ·099	3 40		+ ·099	5 17	
	41	·00		18	·00
	42	3·77		19	2·83
	43	6·39		20	4·44
	44	8·30		21	5·80
	45	9·80		22	6·80
	46	11·10		23	7·70
+ ·006	47	12·20		24	8·40
			+ ·006	25	9·10
— ·099	5 02		— ·099	5 35	
	04	— ·00		36	— ·00
	05	— 2·70		37	—2·35
	06	— 4·65		38	—3·77
	07	— 6·06		40	—5·80
	08	— 7·35	— ·006	45	—8·90
	09	— 8·40	+ ·099	5 46	
	10	— 9·30		47	·00
— ·096	12	—10·90		48	2·10
				49	3·36
				50	4·30
				52	5·73
			+ ·006	56	7·70

In Table 4 I give results for the viscous effect of moderate values of tensile strain on a plan identical with the above. The pull on the strained wire (the normal being No. 15) is indicated in the first column in kilogrames. The maximum pull which these wires will bear was computed to be between 30 kilos. and 50 kilos. It was found to be 45 kilos. in some cases experimentally. Inasmuch as I here apply 8·4 kilos., the pull applied is 17 per cent to 25 per cent of the load producing rupture.

TABLE 4.—*Viscous effect of moderate traction.*

Soft steel wire. $2\rho = \cdot082$ cm.; $l = l' = 30$ cm.; $\theta = \theta' = 30°$; $\tau = \cdot100$.

Pull.	Time.	$10^3 \times (\phi - \phi')/\tau$	Pull.	Time.	$10^3 \times (\phi - \phi')/\tau$
Kilos.	*h. m.*		*Kilos.*	*h. m.*	
0	5 13		4·8	5 59	
	15	·00		6 01	·00
	17	·03		03	·07
	20	·10		06	— ·07
	24	·13		10	— ·13
	29	·17		23	— ·27
	35	·18		31	— ·40
2·4	5 36	·00	8·4	6 32	
	37	·07		47	·00
	38	·13		7 09	— ·27
	40	·23		23	— ·27
	43	·23		21 00	— ·07
	48	·27			
	52	·40			
	58				

The results of Tables 1, 2, and 3 clearly show the marked influence of the drawn strain in effecting diminution of viscosity. Wires drawn only moderately resilient are of the same low order of viscosity as glass-hard wires. Again, if the wires are drawn very resilient the reduction of the viscosity of the originally soft wire is enormous. To eliminate the effect of different degrees of softness, I also drew down a wire after heating in air (Table 3). The results are in accord with Tables 1 and 2.

Some insight into these results is expeditiously obtained by constructing tangents at like time-points of the curves. This is approximately done in the small summary following (Table 5), by subtracting the values of $(\varphi - \varphi')/\tau$ for the beginning and end of the second minute after twisting. Similar values for stretched wire are given in the last two columns, kg. denoting the load.

TABLE 5.—*Digest for the hard and soft wires in Tables 1, 2, 3, and 4.*

θ	τ	Drawn.	Soft.	θ	τ	Drawn.	Soft.
		$\Delta\frac{\phi - \phi'}{\tau} \times 10^3$	$\Delta\frac{\phi - \phi'}{\tau} \times 10^3$			$\Delta\frac{\phi - \phi'}{\tau} \times 10^3$	$\Delta\frac{\phi - \phi'}{\tau} \times 10^3$
30	+ ·10	1·08	·10	30	+ ·10	4·37	·00
30	— ·10	—1·01	—·00	30	— ·09	—4·72	— ·10
100	+ ·10	2·83	·33	100	+ ·09	10·50	·47
100	— ·09	—3·03	— ·33	100	— ·09	— 9·50	

TABLE 5.—*Digest for the hard and soft wires in Tables 1, 2, 3, and 4*—Continued.

θ	τ	Drawn.	kg.	τ	Stretched.
		$\Delta\frac{\phi-\phi'}{\tau}\times 10^3$			$\Delta\frac{\phi-\phi'}{\tau}\times 10^3$
30	+ ·10	+2·62	0	·10	+ ·03
30	− ·10	−2·70	2·4	·10	+ ·06
30	+ ·10	+1·61	4·8	·10	+ ·07
30	− ·10	−1·42	8·4	·10	
30	+ ·10	+1·26			

From this table the small effect of traction in case of loads below 25 per cent of the breaking stress is specially manifest; an effect negligible in comparison with the diminution of viscosity due to the drawn strain. For the sake of orientation I may assume that corresponding values of $\Delta(\varphi-\varphi')/\tau$ for glass-hardness would at 30° be about $1/10^3$ to $2/10^3$—that is, about equal to this quantity in the case of a moderately resilient wire. In general, the results for the drawn strain both at 30° and at 100° corroborate and accentuate the results already obtained for temper[1], so that the further discussion can be made as in my earlier papers, and may be waived here. I add only that the effect of drawing in case of steel is a decrease of the density of the soft metal; for instance,

Rods.	A.	B.	C.
Originally soft	7·76	7·72	7·68
Drawn very resilient . .	7·72	7·64	7·64
Softened after drawing .	7·80	7·73	

It appears that in this respect also the drawn strain and temper are similar.

DATA FOR STRETCHED WIRES.

4. Returning to the case of simple traction, the changes of sign of $(\varphi-\varphi')/\tau$ suggesting increase of viscosity for loads slightly greater than 5 kilos., indicate that here, as in the case of motional annealing due to torsion, the initial effects are an increase of viscosity. Nevertheless, the obscurely small viscous variations due to traction do not admit of interpretation, unless supplemented by data for very much larger loads. Again, it is desirable and quite feasible, by aid of the apparatus discussed above, to operate cyclically; in which case the results must be such as to bear on the lag-quality of solids under stress.

In the following table (6) I have therefore inserted some data for larger pulls. Traction increases successively as far as 90 per cent of the breaking stress. It will be superfluous to give more than a few typical examples; and the tables can be further abbreviated, because in the stress-decreasing phase of the cycles the viscous effect of loads P

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[1] Phil. Mag., 5th. ser., vol. 26, 1888, p. 205 et seq., cf. Bull. U. S. Geol. Surv. No. 73, Chap. III, 1891.

below the maximum employed is nil, § 1, and therefore sufficiently given by the final load zero. To retain a fixed rate of torsion, τ, it is necessary to twist the wires anew after each of the larger loads; in other words, to bring back the same scale-division into the telescope at the outset of each experiment. Otherwise the torsion seriously decreases in consequence of the rapid viscous deformation of the loaded wire.

TABLE 6.—*Viscous effect of cyclic traction.*

Soft steel. $2\rho = \cdot 081$ centimeters; $l = l' = \cdot 30$ centimeters.

P	τ	Time.	$\frac{\phi-\phi'}{\tau}\times 10^3$
Kg.	*Rad.*	*h. m.*	*Rad.*
0	—·10	11 31	
		33	+ ·00
		40	+2·16
		51	+3·35
9	—·10	11 52	
		53	+ ·00
		56	+ ·23
		59	+ ·45
		64	+ ·52
18	—·10	11 64	
		67	·00
		71	— ·12
		83	— ·37
27	—·10	12 24	
		27	— ·00
		30	— ·37
		37	— ·48
36	—·10	12 39	
		40	— ·00
		46	—1·64
		53	—2·53
40	—·10	12 53	
		55	·00
		60	—2·08
		65	—5·07
		78	—9·62
40	(*)	1 22	$(\phi-\phi')\times 16^6$
		23	-- 0
		25	—1440
		27	—1750
		30	—2120
40	(*)	1 32	
		35	— 0
		37	— 200
		39	— 390
0	(*)	1 51	
		52	·00
		55	+ ·30
		3 30	+1·10
0	+·13	10 22	
		28	·00
		31	·00
		36	·00
		44	·19
9	+·13	10 45	
		46	·00
		49	·38
		52	·55
		55	·63
18	+·13	10 56	
		59	·00
		61	·05
		65	·08
		68	·12
27	+·13	11 09	
		10	·00
		13	·45
		16	·78
		19	1·04
36	+·13	11 20	
		21	·00
		24	1·90
		27	3·37
		30	4·61
40	+·13	11 31	
		34	·00
		36	2·71
		38	4·84
		41	7·58
0	+·13	11 42	
		45	·00
		50	·09
		60	·09
0	+·13	12 01	
		04	·00
		09	—·13
		13	—·27

* Twisted again.

TABLE 6.—*Viscous effect of cyclic traction*—Continued.

Soft steel. $2\rho = \cdot 081$ centimeters; $l = l' = \cdot 30$ centimeters.

P	τ	Time.	$\frac{\phi - '\phi}{\tau} \times 10^3$	P	τ	Time.	$\frac{\phi - \phi'}{\tau} \times 10^3$
Kg.	*Rad.*	*h. m.*	*Rad.*	*Kg.*	*Rad.*	*h. m.*	*Rad.*
20	+ ·13	12 14		38	+ ·13	12 45	
		15	·00			47	·00
		18	·00			50	1·53
		22	·05			53	2·67
		24	·07			56	3·79
		28	·09			60	5·21
29	+ ·13	12 30		42	+ ·13	1 01	
		31	·00			04	·00
		33	·11			07	9·1
		36	·25			10	14·9
		40	·33			13	19·8
		44	·44			17	25·1
				Wire breaks at P = 46 kg.			

In adding the successive loads care was taken to avoid vibration and jarring; but without special machinery it is impossible to protect the system completely against it. To this cause I attribute certain irregularities of sequence which these and others of my results exhibit. Their general significance is none the less definite. The effect of traction is diminution of viscosity, increasing at an accelerated rate in proportion as stress approaches the limit of rupture. Indeed, by sufficiently increasing stress, viscosity may be diminished in any degree whatever. The singularly curious feature of these experiments is this: that with the removal of load the viscous effect of traction almost entirely vanishes. It is in this respect that the present experiments bear directly on the truth of Maxwell's theory; for it is only during the interval within which conditions favorable to molecular break-up are *forcibly* maintained that the wires exhibit a low order of viscosity of a sufficiently marked degree to compare with the viscous effect of drawn strains and of temper, where instabilities are structurally retained.

It follows, in general, that slight applications of mechanical treatment (twisting, traction, etc.), inasmuch as they decrease in number the motionally unstable configurations of the soft wire, increase viscosity (motional annealing). If this treatment is intensified beyond a critical stage—in other words, if stress is increased sufficiently beyond the limits of resilience and toward the limits of rupture—then viscosity is again seriously decreased. For the action of stress has now become such as to introduce its own specific instability, whereby viscous deformation is again promoted.

INFERENCES.

5. Having thus substantiated the remarks of § 1, and shown that the accordant results of the earlier observers and my own are such as fol-

low naturally from Maxwell's theory, it is expedient to give a graphic representation of the more important differential data (i. e., differences between strained and soft metal for each case of stress) in hand. In figure 2 the viscous deformation $(\varphi-\varphi')/\tau)$ produced by the action of a fixed rate of twist τ, is represented as ordinate, time as abscissa. The material is steel, the originally soft state of which has been transformed by temper (glass-hardness), drawn strain (wire-plate), tensile strain, and torsion respectively. Curves are given for intense values and for moderate values of stress. The nature of the problem precludes greater definiteness as to stress data. In case of traction infinitesimally below the point of rupture, for instance, viscous deformation would occur with such extreme rapidity that its diagrammatic representation would be a vertical line.

Again, in case of traction of sufficiently small value, the curve would be a horizontal line coinciding with "soft," or even a curve below it (motional annealing). In a measure this is true of the other strains; and I have therefore expediently inserted the values for deformations actually found.

The general outcome of the present paper is this, that the effect of strain of whatever kind, applied in sufficient intensity to homogeneous soft steel, is marked diminution of viscosity. Again, inasmuch as the underlying cause of viscous deformation is the occurrence of unstable configurations the number of which is being reduced in the course of viscous motion, Maxwell's theory naturally suggests the applicability of exponential equations for the description of the time relations of such motion. From another point of view it appears that the loss of viscosity experienced by a given metal, under action of a given kind of strain, may not inappropriately be used as a measure of its intensity. Finally, the curious observation, that in all the cases given loss of viscosity has taken place simultaneously with increase of hardness, is one of the suggestive results of the experiments made.

Quite recently Auerbach,[1] in applying a method for the absolute evaluation of hardness due to Hertz, has shown that hardness and elasticity are associated quantities, i. e., quantities between the corresponding variations of which a close agreement is maintained irrespective of the body operated on. Hence the above results show a fundamental distinction between viscosity and elasticity.

From experiments made on the behavior of iron in passing through the temperature of recalescence Osmond[2] was led to conclude that all the phenomena of hardness are due to a second or β variety of iron. This β iron may be formed from ordinary or α iron, either spontaneously by heating above a certain high temperature, below which, however, it is unstable and passes back to α iron on cooling

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[1] Auerbach: Wied. Ann., vol. 43, 1891, p. 61. Other references are there given.

[2] Osmond: Annales des Mines, July-August, 1888, "Introduction," and elsewhere. Cf. Bull. U. S. Geol. Surv. No. 73, p. 51, 1891.

except under certain conditions, or β iron may be formed artificially by the action of pressure of any kind applied below the critical temperature in question. The presence of carbon (steel) and rapid cooling is specially favorable to the production of β iron, and the presence of

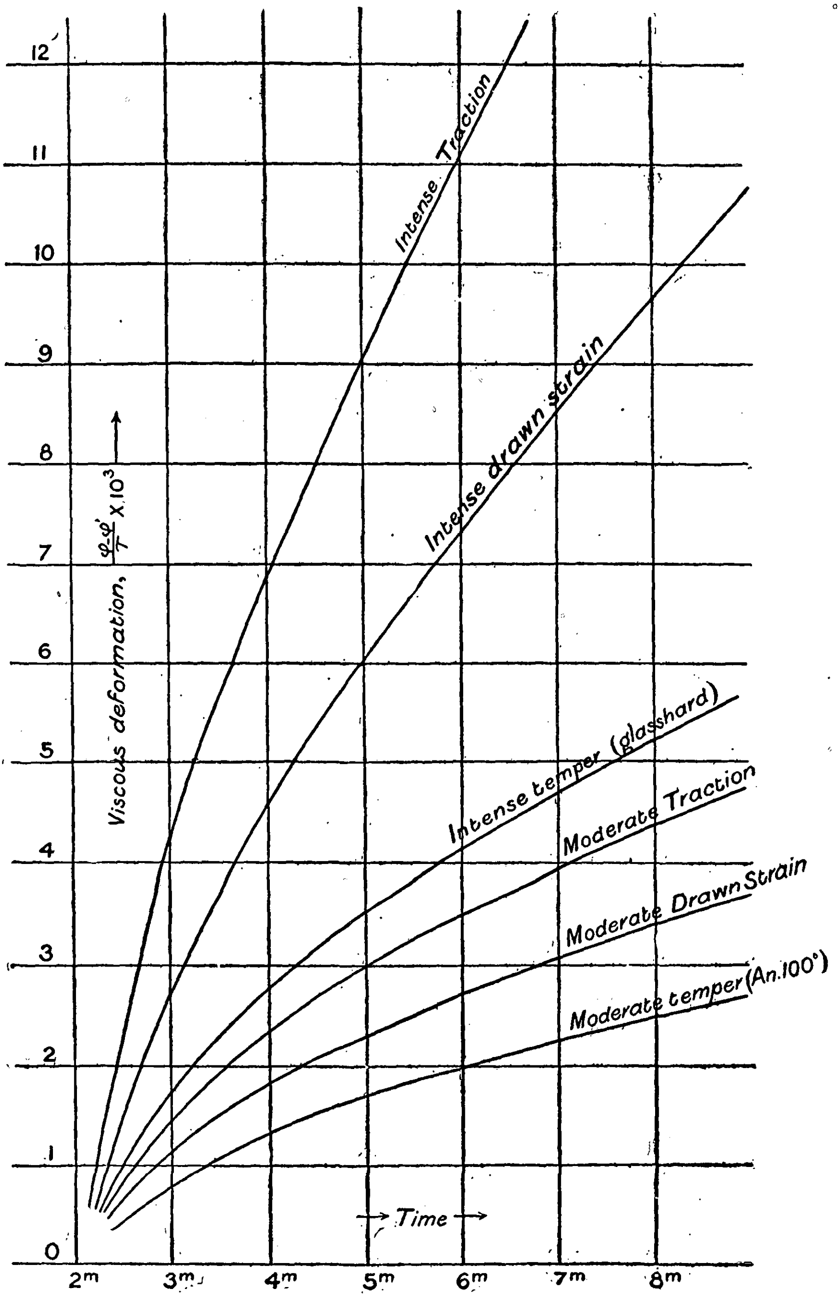

Fig. 2.—Time variation of viscous deformation, in case of soft steel transformed by temper, drawn-strain, traction, and torsion, respectively. The abscissa represents the soft or unstrained wire.

this substance manifests itself in the resulting hardness of the metal. Now it is to be observed that the above observation on the similarity of viscous effects of all kinds of strain, whether tempered or mechanically applied, is in harmony with Osmond's theory. Again, the acknowledged instability of β iron at ordinary temperatures supplies the requisite unstable configurations in virtue of which, following Maxwell's theory, viscosity is reduced. This theory of Osmond, however, either proves too much or it is a suggestive working hypothesis relative to the behavior of other metals. For the results of Streintz, Tomlinson, and myself, cited above, show that in most if not all metals viscosity is reduced by the presence of marked intensity of mechanical strains. Certainly metals are capable of being hardened by traction, the draw plate, torsion, etc., although no phenomenon corresponding to Gore's phenomenon in iron has been observed. Osmond's theory of a change of molecule of iron by mechanical action therefore calls for experiments relative to the definite discovery of the α and β varieties of metals other than iron, nickel, and a few more, before the standpoint taken can be maintained.

An important inquiry is thus suggested which would lead ulteriorly to a test of Osmond's theory: It is to be found whether the maximum of drawn strain which the wire of a given metal can retain is (cæt. par.) a function of the viscosity of the metal; or whether the strain retained is largely independent of viscosity and subject to other conditions. In the last case retention would be conditioned by a chemical mechanism, and Osmond's theory would therefore be substantiated at once.

I may state in concluding that Osmond's views are not wholly new, having been suggested in their general bearings in a remarkable thermoelectric investigation by F. Braun.[1]

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[1] F. Braun: Phil. Mag. (5), vol. 19,1885, p. 503, § 8.

CHAPTER II.

THE TWO SPECIES OF MOLECULAR BREAK-UP WHICH PROMOTE VISCOUS DEFORMATION.

INTRODUCTORY.

6. Following the argument which underlies Maxwell's theory of solid viscosity experimentally, I was obliged to take cognizance of two causes which promote viscous deformation in solids.[1] For any structure will give way under impressed conditions of stress, as a whole or in part, because either the cements or the bricks are insufficiently strong to withstand it. Similarly the underlying cause of viscous motion is either such structural change in which groups of molecules pass without loss of identity from an initial to a final configuration, or it is a break-up superinduced by the disintegration of one or more molecules of each group. Whichever the change may be, it must, from the nature of the problem in general, be distributed uniformly throughout the mass of the solid (§ 14). Even without stress the said change may result from secular subsidence. Moreover it is conceivable that molecular disintegration may occur in such a way as to elude detection.

Now I have since been able to prove experimentally that in glass-hard steel a change of the viscous quality may be obtained as the result of at least *two* distinct kinds of structural change, probably as the result of the two kinds of break-up in question. The present chapter purposes to show this by aid of the phenomena of accommodation, or motional annealing, as they may be called more uniformly in keeping with the following work.

MOTIONAL ANNEALING DEFINED.

7. The term annealing or tempering, in its most general sense, refers to a process by which strained solid structure, whether maintained by mechanical or chemical causes, is changed to isotropic structure. In viscosity, inasmuch as strained structure is ultimately accompanied by molecular instability, annealing is a process by which viscosity is increased; and from this point of view annealing need have no direct reference to exposure to temperature. Hence I have designated by the term motional annealing all such forced molecular motion to and fro, in virtue of which the molecules of a thoroughly soft solid are brought into new relations to each other, to the effect that viscosity is increased at

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[1] Phil. Mag., November, 1888.

the expense of the motionally less stable configurations of the soft solid. There may appear to be some incongruity in the term, inasmuch as the solid motionally acted on always experiences strain; it is not the strain, however, but the *increment of viscosity* of the solid, to which the term refers.[1]

Again, in order that a solid may be motionally annealed the mechanical treatment (torsion, traction, etc.) must be applied *below* a certain critical limit of intensity. Otherwise this treatment introduces its own specific instability; and in proportion as stress is indefinitely increased the viscosity of the solid may now be reduced in any measure. Further justification of the term is to be given in §§ 11, 14. At present it is more expedient to indicate the points of crucial difference between motional annealing and thermal annealing in their effect on steel in the glass-hard state.

STRAIN, ELECTRIC RESISTANCE, AND VISCOSITY.

8. When glass-hard steel is annealed at 100° the effect is a decided increase of viscosity amounting to almost one-half of the total viscous interval, hard-soft.[2] This marked increment of viscosity is accompanied by an equally striking electrical effect.[3] For it has been shown that the specific resistance of hard steel diminishes as much as 15 per cent as the result of annealing at 100°. Finally, since the electrical effect is a sufficient indication of the changes of volume (decrement) and of carburation, it appears conclusively that the underlying cause of the increase of viscosity here in question is a disintegration of the unstable carbide molecule of steel.

TEMPER, ELECTRIC RESISTANCE, AND VISCOSITY.

9. Again, an increment of the viscosity of glass-hard steel comparable in magnitude with that of annealing at 100° may be obtained without heat. It is merely necessary, for instance, to apply to the glass-hard wire large enough rates of twist, a sufficient number of times alternately, in opposite directions. This method of increasing viscosity has no electrical concomitant comparable with the electrical effect of § 8. Hence the underlying cause of the observed increase of viscosity in this case is probably not a disintegration of the carbide molecule of steel, or, at least, a disintegration quite unlike that of the foregoing instance.

DATA RELATIVE TO TEMPER, ELECTRIC RESISTANCE, AND VISCOSITY.

10. In the following tables (7 and 8) I give the data necessary to substantiate § 9. The method[4] of experiment being identical with the

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[1] Phil. Mag., 5th ser., vol. 26, 1888, pp. 199 to 203.

[2] Am. Jour. Sci., 3d ser., vol. 33, 1887, p. 26; Phil. Mag., 5th ser., vol. 26, 1888, p. 188, et seq.

[3] Bull. U. S. Geological Survey, No. 14, p. 49, 1885.

[4] Phil. Mag., 5th ser., vol. 26, 1888, pp. 189 to 191. The use of differential methods premises that the viscous deformations of all the wires to be compared are similar time functions. That this is the case must be verified preliminarily by some absolute method.

one described in verifying § 8, I need only to call to mind here that my normal steel wire (maximum viscosity) and the fresh glass-hard wire (minimum viscosity) were countertwisted; that the ends of the vertical system were fixed, and a mirror-index placed near the middle, at the junction of the two wires.[1] Cf. Fig. 1, § 3. Table 1 contains the results for viscosity, both wires being at the same temperature θ. The impressed rate of twist is given in radians under τ, and the permanent torsion observed at the close of each experiment under $2(\varphi + \varphi')$. Since the lower end of the system was twisted 360°, $\tau + 2(\varphi + \varphi'), = 2\pi/L$, where L is the length of the two wires. Finally, $(\varphi - \varphi')/\tau$ is the viscous motion at the index, per unit of τ, per unit of L, at the time specified. In other words, 2φ and $2\varphi'$ refer to the hard and the soft wires, respectively, and denote angular viscous motion of one right section relatively to another, when their distance apart is 1 cm. of length of wire. $(\varphi - \varphi')/\tau$ need not be independent of τ. (§ 13.)

Table 7 indicates that the wires were twisted eight times alternately in opposite directions. Before and after each series of viscous measurements in Table 7 the resistance of the glass-hard wire was measured by a special device utilizing Matthiessen and Hoskin's method. These results are given in Table 8, where r_t is the observed resistance in microhms, $\triangle r_t$ the variation from the final value, $r_t = 39500$.

TABLE 7.—*Viscous effect of motional annealing. Glass-hard steel.*

$\theta = 29$. L = 30 cm. + 30 cm. Diameter of wires, $2\rho = \cdot 081$ cm.

Twist No.	$\frac{\tau}{2(\phi + \phi')}$	Time.	$\frac{\phi - \phi'}{\tau} \times 10^3$	Twist No.	$\frac{\tau}{2(\phi + \phi')}$	Time.	$\frac{\phi - \phi'}{\tau} \times 10^3$
		h. m.				*h. m.*	
1.	+·0992	2 25		5.	+·1021	3 40	
		30	+ ·00			42	+ ·00
		32	·94			44	·68
		35	1·99			47	1·38
		38	2·79		+·0026	52	2·19
	+·0055	46	4·45				
2.	—·0983	2 49		6.	—·1018	3 55	
		51	— ·00			57	— ·00
		53	—1·95			59	— ·74
		56	—3·97			62	—1·44
	—·0064	63	—5·93		—·0029	67	—2·39
3.	+·1021	3 07		7.	+·1018	4 09	
		09	+ ·00			11	·00
		11	1·01			13	·64
		14	1·99			16	1·28
	+·0026	21	3·36		+·0029	20	1·89
4.	—·1021	3 24		8.	—·1018	4 23	
		27	— ·00			25	— ·00
		29	— ·91			27	— ·64
		32	—1·85			30	—1·28
	—·0026	37	—3·06		—·0029	37	—2·32

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[1] See Bull. U. S. Geol. Survey No. 73, 1891, pl. I, p. 54.

TABLE 8.—*Electrical effect of motional annealing.*

Glass-hard steel, $2\rho = \cdot 081$ cm.

Twist No.	τ	r_t	Δr_t	Twist No.	τ	r_t	Δr_t
0.	0	39550	+ 50	5.	—·102	39560	+60
1.	—·099	39380	—120	6.	+·102	39530	+30
2.	+·098	39350	—150	7.	—·102	39500	+00
3.	—·102	39570	+ 70	8.	+·102	39510	+10
4.	+·102	39430	— 70				

DISCUSSION OF RESULTS.

11. The results of Table 7 are in excellent accord with my earlier data; and the oscillatory march of the viscous increment can be represented in the same way. If the tangents be constructed at the same time-point, in each of the curves of Table 7 there appears to be some similarity between the march of these results $(\triangle(\varphi-\varphi')/\tau)$ and the corresponding march of r_t in Table 8. But interpreted by the data of § 7, this similarity is only qualitative in kind. In other words, whereas the increment of viscosity due to successive alternations of twist is decidedly greater than one-half of the increment of viscosity due to annealing glass-hard steel at 100°, it appears that the electrical effect in the first instance (motional annealing) is practically negligible in comparison with the electrical effect of thermal annealing. In Table 8 the total interval of variation of $\triangle r_t$ is about one-half per cent of r_t; on the other hand, the variation of r_t due to annealing at 100° is from 10 per cent upward. It follows that in glass-hard steel there are two distinct ways in which viscosity may be appreciably increased, a result corroborating §§ 8, 9. Again, if the possibilities of viscous motion are to be fully given, it is essential to postulate groups of atoms, as well as the somewhat less definite groups of molecules, both varying in degrees of stability from point to point of the solid mass. Hence slight positional change of the elements of the atomic configurations, or of the molecular configurations, due either to stress not exceeding a critical value or to mere secular subsidence, must in general involve an augmentation of the viscous quality.

DATA FOR CYCLIC TWISTING.

12. Having arrived at this result I desire to inquire somewhat more in detail into the viscous relations of the motional effect, §§ 9, 10. This is attempted in Table 9, in which torsional stress is applied cyclically. The viscous behavior is studied at each of these successive stages of increase or decrease, as shown in the first column, τ, of the table. As before, the length of the system of two wires, $L = l + l' = 30$ cm. + 30 cm.; diameter, $2\rho = \cdot 081$ cm. The final column, $\triangle(\varphi-\varphi')$, being the detorsion from the beginning to the end of the first minute after twisting, may be taken as an index of the rate of deformation. In the first and second cycles twist is imparted positively; in the third cycle negatively. To follow the sequence of observations it is sufficient to consult the time column.

TABLE 9.—*Viscous deformation in case of cyclic twisting.*

FIRST CYCLE.

Twist increasing.					Twist decreasing.			
Rate of twist, τ	Time.	$(\phi-\phi')\times10^6$	$\frac{\phi-\phi'}{\tau}\times10^3$	$\Delta(\phi-\phi')\times10^6$	Rate of twist, τ	Time.	$(\phi-\phi')\times10^6$	$\Delta(\phi-\phi')\times10^6$
						h. m.		
·000					·000	12 31	....	—10
						32	0	
						33	— 10	
						34	— 20	
						35	— 27	
						1 18	—107	
						30	—120	
	h. m.							
·009	10 36	....	....	3	·009	12 26	....	— 8
	37	0	·0			27	0	
	38	3	1·1			28	— 8	
	39	5	1·5			29	— 15	
	40	6	1·9			30	— 21	
·017	10 41	....	....	9	·017	12 21	....	— 5
	42	0	·0			22	0	
	43	9	1·4			23	— 5	
	44	15	2·8			24	— 12	
	45	20	3·2			25	— 17	
·026	10 46	....	....	14	·026	12 16	....	— 7
	47	0	·0			17	— 0	
	48	14	1.5			18	— 7	
	49	23	2·5			19	— 12	
	50	27	2·8			20	— 15	
·035	10 51				·035	12 11	....	— 7
	52	0				12	0	
	53	31				13	— 7	
	54	51				14	— 13	
	55	67				15	— 15	
·043	10 56				·043	12 06	....	— 5
	57	0				07	0	
	58	45				08	— 5	
	59	77				09	— 8	
	60	100				10	— 13	
·052	11 01				·052	12 01	....	— 3
	02	0				02	0	
	03	36				03	— 3	
	04	69				04	— 9	
	05	103				05	— 11	

TABLE 9.—*Viscous deformation in case of cyclic twisting*—Continued.

FIRST CYCLE—Continued.

Twist increasing.					Twist decreasing.			
Rate of twist, τ	Time.	$(\phi-\phi')\times10^6$	$\frac{\phi-\phi'}{\tau}\times10^3$	$\Delta(\phi-\phi')\times10^5$	Rate of twist, τ	Time.	$(\phi-\phi')\times10^6$	$\Delta(\phi-\phi')\times10^6$
	h. m.					*h. m.*		
·061	11 06				·061	11 56	....	− 7
	07	0				57	0	
	08	60				58	− 7	
	09	100				59	− 7	
	10	133				60	− 9	
·070	11 11	....	....	97	·070	11 51	....	− 5
	12	0	·0			52	0	
	13	97	3·8			53	− 5	
	14	153	6·1			54	− 5	
	15	207	8·2			55	− 5	
·078	11 16	....	....	100	·078	11 46	....	− 2
	17	0	·0			47	0	
	18	100	3·5			48	− 2	
	19	167	5·9			49	− 2	
	20	237	8·3			50	− 1	
·087	11 21	....	....	117	·087	11 41	....	+ 3
	22	0	·0			42	0	
	23	117	3·7			43	+ 3	
	24	197	6·3			44	+ 7	
	25	263	8·3			45	+ 10	
·096	11 26	....	....	137	·096	11 36	....	+ 8
	27	0	·0			37	0	
	28	137	3·9			38	+ 8	
	29	233	6·8			39	+ 21	
	30	307	8·9			40	+ 31	
·105	11 31	....	....	167				
	32	0	·0					
	33	167	4·4					
	34	280	7·4					
	35	397	9·6					

TABLE 9.—*Viscous deformation in case of cyclic twisting*—Continued.

SECOND CYCLE.

Twist increasing.					Twist decreasing.			
Rate of twist, τ	Time.	$(\phi-\phi')\times10^6$	$\frac{\phi-\phi'}{\tau}\times10^3$	$\Delta(\phi-\phi')\times10^6$	Rate of twist, τ	Time.	$(\phi-\phi')\times10^6$	$\Delta(\phi-\phi')\times10^6$
						h. m.		
·0					·0	2 26	....	— 9
						27	— 0	
						28	— 9	
						29	— 17	
						30	— 23	
	h. m.							
·017	1 31	....	....		·017	2 21	....	—12
	32	0	·0			22	— 0	
	33	5	·7			23	— 12	
	34	7	1·2			24	— 19	
	35	11	1·8			25	— 25	
·035	1 36	....	....	7	·035	2 16	....	— 5
	37	0	·0			17	— 0	
	38	7	·5			18	— 5	
	39	13	1·1			19	— 10	
	40	15	1·2			20	— 15	
·052	1 41	....	....	7	·052	2 11	....	— 9
	42	0	·0			12	— 0	
	43	7	·3			13	— 9	
	44	10	·5			14	— 11	
	45	17	·9			15	— 14	
·070	1 46	....	....	7	·070	2 06	....	— 7
	47	0	·0			07	— 0	
	48	7	·3			08	— 7	
	49	19	·7			09	— 7	
	50	30	1·2			10	— 7	
·087	1 51	....	....	15	·087	2 01	....	— 2
	52	0	·0			02		
	53	15	·5			03	— 0	
	54	30	·9			04	— 2	
	55	41	1·3			05	— 4	
·105	1 56	....	....	67				
	57	0	·0					
	58	67	1·9					
	59	120	3·2					
	60	170	4·5					

TABLE 9.—*Viscous deformation in case of cyclic twisting*—Continued.

THIRD CYCLE.—TWIST IN OPPOSITE DIRECTION.

Twist increasing.					Twist decreasing.			
Rate of twist, τ	Time.	$(\phi-\phi')\times10^6$	$\frac{\phi-\phi'}{\tau}\times10^3$	$\Delta(\phi-\phi')\times10^6$	Rate of twist, τ	Time.	$(\phi-\phi')\times10^6$	$\Delta(\phi-\phi')\times10^6$
	h. m.					*h. m.*		
·017	3 24	....	....	12	·0	4 17	....	—28
	25	0	·0			18	— 0	
	26	12	1·9			19	— 28	
	27	19	3·0			20	— 45	
	28	25	3·9			21	— 63	
	29	28	4·6					
.035	3 30	....	....	13				
	31	0	·0					
	32	13	1·1					
	33	32	2·5					
	34	37	2·9					
·052	3 35	....	....	43				
	36	0	·0					
	37	43	2·3					
	38	77	4·1					
	39	103	5·5					
·070	3 40	....	....	97	·070	3 50	....	— 1
	41	0	·0			51	— 0	
	42	97	3·8			52	— 1	
	43	163	6·5			53	— 1	
	44	213	8·5			54	+ 2	
·087	3 45	....	....	147	·087	4 00	....	+ 5
	46	0	·0			01	0	
	47	147	4·7			02	+ 5	
	48	240	7·6			03	+ 14	
	49	307	9·8			04	+ 23	
·096	3 55	....	....	117	·096	4 10	....	0
	56	0	·0			11	+ 0	
	57	117	3·4			12	+ 0	
	58	207	6·0			13	+ 10	
	59	273	7·9			14	+ 27	
·105	4 05	....	....	135				
	06	0	·0					
	07	135	3·6					
	08	240	6·4					
	09	313	8·3					

DISCUSSION OF RESULTS OF CYCLIC TWISTING.

13. *The marked feature.*—The first result given by these data is obtained by comparing $\varphi-\varphi'$ and $(\varphi-\varphi')/\tau$, showing that the latter quantity is not independent of τ. Nor can it be asserted that the change of $(\varphi-\varphi')/\tau$ with increasing τ is retarded. It follows that comparable values of $(\varphi-\varphi')/\tau$ are only obtained by keeping τ nearly constant, as has been done in all my experiments.

Again, the large variations of $(\varphi - \varphi')$ in the direct or stress-increasing phase of the cycles, as compared with the corresponding variations in the retrograde or stress-decreasing phase of the cycles, together with a repetition of the whole phenomenon on a smaller scale for succeeding cycles of the same sign, are features of these experiments. When the sign of the twist is reversed, cycles which exceed the original one in magnitude are obtained. These in their turn dwindle on repetition of like signs of τ. Finally, the influence of residual action in case of retrograde cycles appears more clearly in proportion as stress approaches zero. On the other hand, the circumflex contours of the earlier retrograde curves (τ decreasing from ·105) is not a mere error of observation, but results from superposition of direct and residual phenomena. This is specially marked in the third cycle, where stress, after $\tau = \cdot 087$, was applied in a zigzag way, viz:

$$\tau \times 10^3 = 87, 70, 96, 87, 105, 96.$$

14. *Analogy with thermal annealing.*—The clue for the interpretation of the above complex phenomena as a whole is suggested by the data for $\Delta\,(\varphi - \varphi')$. It then appears that the viscous behaviour of the wires is intimately connected with the amount of permanent set imparted during the period of action of stress. From this point of view the phenomena become not only strikingly analogous to thermal annealing in case of temper, but of special importance as regards their bearing on Maxwell's theory. The following description[1] applies, mutatis mutandis, to both classes of phenomena:

(1) The viscous deformation (annealing effect) of any stress (temperature) acting on glass-hard steel increases gradually at a rate diminishing through infinite time; diminishing very slowly in case of low stress (temperature); diminishing very rapidly at first and then again slowly in case of high stress (temperature); so that the limit of permanent deformation is approached asymptotically.

(2) The ultimate viscous deformation (annealing effect) of any stress τ (temperature t), is independent of preexisting effects of the stress τ' (temperature t'), and is not influenced by subsequent application of stress τ' (temperature t'), provided $\tau > \tau'$ ($t > t'$). In case of incomplete deformation (partial annealing) induced by stress τ (temperature t), this law applies more fully as the ultimate effect of τ (t) is more nearly reached. Again, the effect of τ' succeeding τ (t' succeeding t) is more nearly nil as the effect of $\tau > \tau'$ ($t > t'$) approaches completeness.

To discern the cause of this detailed analogy it is sufficient to call to mind, (1) that in thermal annealing viscous deformation is produced by thermal diminution of viscosity under conditions of the initially given stress stored up in the tempered solid; in motional annealing by increase of the mechanical stress applied from without under conditions of initially given viscosity. Finally, (2) the configurations, molecular

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[1] Cf. Phil. Mag., 5th ser., vol. 26, 1888, p. 214.

or atomic, which just break up under the action of stress τ or temperature t, respectively, are necessarily limited by a higher order of stability, and are greater in number than those just surviving under less intense conditions of stress or temperature. This is the crucial feature of the analogy. However unlike the instabilities may be in the two cases of motional and of thermal annealing, however unlike the treatment to which they are here respectively subjected, its effect in *modifying the occurrence* of instability is similar, and hence the similarity of viscous results.

So far as I have observed, however, residual phenomena are absent in thermal annealing of glass-hard steel, and this is a point of difference between the break-up of atomic groups and molecular groups. The former are not reconstructed. Again, in motional annealing for increasing rates of twist, thick wires show viscous deformation at earlier dates than thin wires. The break-up commences at the external surface, where stress is most intense, and proceeds thence to the axis, where stress is least. The history of motional annealing is therefore essentially dependent on the dimensions of the deformed wire and varies for different values of radius. I pointed out[1] that in soft iron the limits of torsional resilience were reached when the obliquity of the external fiber (shear) somewhat exceeds .003 radians. Finally, the ultimate annealing effect (time $= \infty$) of any temperature t acting on glass-hard steel increases at a retarded rate with temperature, and practically reaches the limit of variation below 350°. In case of motional annealing stress may be applied in any degree from without, and increasing effects obtained limited only by the given degrees of resilience or of brittleness. Nevertheless, if the wire admits of permanent set, the analogy pursued may be pushed even to this extreme detail. For, just as in the case of thermal annealing above 350°, no further marked effects are produced, because the intensity of stored stress is invariably below the value of viscosity; so in case of motional annealing, when stress surpasses the limits of resilience, further increment of marked consequence is no longer elastically retained.

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[1] Am. Jour. Sci., vol. 34, 1887, p. 183.

CHAPTER III.

THE EFFECT OF MECHANICAL STRAIN ON THE CARBURATION OF STEEL.

INTRODUCTORY.

15. *Drowne's experiments.*—I shall, in this chapter, endeavor to discuss the nature of some shortcomings of the present methods for the estimation of uncombined carbon in addition to the subject matter of the superscript. Among earlier investigators Dr. Thomas Drowne[1] has made similar observation with reference to cast iron. The stimulus of Drowne's work was a remark of Bell's, stating that white and gray pig iron differ only in the magnitude of graphitic crystals contained, which crystals are fine grained in white pig, and coarse grained in gray pig. To disprove this assertion Drowne cast a sample of iron in a chill mold,[2] thus obtaining both the white and the gray variety. Analyses showed that while these two parts of the same casting did not differ much in total carbon, the free carbon in the gray iron was more than twice as great in amount as the free carbon in the white iron. He thus obtained strong evidence against Bell's statement. Drowne then proceeded to vary the method of treatment by varying the solvent and by boiling. He infers that the carbide is not decomposed except by boiling, and accentuates the crudeness of the analytical methods.

16. *The present method.*—The above pages have clearly shown that the underlying cause of viscous deformation is either a break-up of atomic or of molecular configuration. The former phenomenon admits of direct proof and does occur in glass-hard steel. The molecular break-up is less easily verifiable, and can not be as clearly defined as the other. I have therefore been tempted to question whether, even in the case of viscous deformation induced by mechanical strains, the underlying break-up is a mere rearrangement of molecules. (Cf. § 9.)

Among the more promising methods for deciding this question, the plan adopted in the discussion of annealing phenomena[3] suggests itself. An exceedingly intimate intermixture of carbon and iron is here presented. Indeed Matthiessen considered it a solidified solution or mix-

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[1] Drowne: Trans. Am. Inst. Mining Engineers, vol. 3, 1874–'75, pp. 41–44.

[2] I may refer here to a similar experiment of Karsten's (Eisenhüttenkunde, Bd. I, 3 Aufl., 1841. p. 581, et seq.) from which the distinction between combined and uncombined carbon was originally derived.

[3] Barus: Bull. U. S. Geol. Survey, No. 73, Chap. III, 1891.

tures of these. Hence the possibility of chemical changes of configuration superinduced by mechanical stress (wire-pulling, torsion, flexure, traction, compression) applied from without, is favorably open to experiment. Put in its simplest form, the problem is a determination of the variation of the amount of the uncombined carbon in steel, produced by stress; for it may be plausibly argued, I think, that such disintegration of molecule as is here in question could hardly take place without the accompaniment of a carburation effect.

METHOD OF EXPERIMENT.

17. The method of procedure, apart from its extreme tedium, is sufficiently simple. A soft wire of proper length is cut into halves, one of which is dissolved without further treatment, the other drawn down to as small a diameter as feasible and also dissolved. The two samples are then tested for uncombined carbon. I used the customary process described by Blair in its most complete form. The samples were dissolved in cold dilute acid, then boiled, after which the carbon was collected on Gooch's asbestos filter, duly washed with dilute HCL and hot water, KOH, alcohol and ether. It was thereupon dried at a temperature of at least 160° for a sufficient time, cooled in a desiccator, and the difference in weight of the Gooch crucible before and after ignition in oxygen estimated as carbon. This is not as accurate a process as the regular combustion method usually prescribed. But it is far more expeditious; and the errors made in weighing carbon directly are of very much smaller moment than the solution and other errors which I will point out below. Indeed the validity of the whole method stands seriously in question, in a number of fundamental particulars; and so long as these have not been surely cleared away, refinements of carbon measurement are obviously absurd.

RESULTS OBTAINED.

18. My results are given in the following Table 10. To understand them fully, introductory remarks as to the structure of the soft steel used in each case are essential. In my first experiments (rods Nos. 1 and 2 for instance), I drew down the whole wire; then I softened one-half of it after drawing, by annealing at red heat *in air*. On dissolving, the drawn wires were very much more intensely attacked than the freshly softened wires; so that the beaker containing drawn wires is turbid and black with carbon before the other hardly shows traces of carbon precipitate. This result is exceedingly striking and uniform, and I at first inferred that the effect of drawing is necessarily a transformation of carbon in steel from the combined to the uncombined state. And yet this conclusion, as I afterwards found, does not at all follow. The effect of annealing at red heat on the carbon in the steel varies enormously with the details of the method. In other words, steels of a given kind and nominally soft, may nevertheless differ remarkably in internal structure. If we start with soft steel, annealed by the commercial method of excessively slow cooling, and then draw the wires down, it can not be assumed that the part of the drawn wire which is annealed at red heat and cooled in air after drawing, is identical with the wire before drawing. Indeed, since the rate of cooling increases as the diameter decreases, it follows that two wires annealed at red heat in air must differ in degrees of softness and carburation even if all other conditions are the same. I desire to emphasize this point for it indicates the first difficulty with which I had to contend.

TABLES.

19. In the Table I have, therefore, inserted the treatment and temper of the wire before drawing in the wire plate, as well as after drawing. The radius ρ of the wire is also given for each case.

M is the mass of steel dissolved, in grammes. A larger amount would have been desirable, but the rods of best Stubb's steel come in short lengths (33^{cm}), and as the drawing of each new length nearly doubles the labor, I did not care to operate upon greater masses (*M*) of steel. The carbon contained in the *M* grammes in question is given under *m*, also in grammes, and the final columns contain the values of m / M.

Excepting numbers 27 and 28, the first thirty-four measurements were made with a view to testing the steel; the next twenty-one (numbers 35 to 56) chiefly with a view toward testing the method. In the final measurements, the steel again is chiefly considered.

TABLE 10.—*Graphitic carbon in soft and in drawn steel.*

[S, annealed from red heat, with very slow cooling (commercial). SA, heated to redness and cooled in air. GH, glass-hard. An, annealed at 500°. Dr, fresh drawn, usually from diameter $=2\rho=0{\cdot}13^{cm}$ to $2\rho=0{\cdot}08^{cm}$.]

Before drawing.			Before dissolving.		M	$m\times10^3$	$\frac{m}{M}\times10^3$	No.
Original condition.	Final condition.	$2\rho\times10^3$	Condition.	$2\rho\times10^3$				
S	S	130	Dr	80	3·10	18·3	5·9	1
S	S	130	SA	80	3·16	15·4	4·9	2
S	S	130	Dr	80	3·17	15·9	(?)5·0	3
S	S	130	An. 1^h	80	3·14	17·4	5·5	4
S	S	130	An. $1\frac{1}{2}^h$	80	2·30	16·5	5·5	5
S	S	130	SA	80	2·91	lost	....	6
S	SA	130	Dr	80	3·04	17·2	5·6	7
S	SA	130	SA	80	2·98	18·0	6·0	8
GH	SA	130	SA	130	3·15	14·9	4·7	9
GH	SA	130	Dr	90	2·96	18·2	6·1	10
S	S	130	S	130	3·25	27·1	8·3	11
S	SA	130	SA	130	3·21	22·3	6·9	12
GH	SA	130	SA	130	3·17	16·7	5·3	13
GH	SA	130	Dr	80	2·96	17·4	5·9	14
GH	SA	130	SA	130	3·22	19·7	6·1	15
GH	SA	130	Dr	80	2·74	14·9	5·4	16

TABLE 10.—*Graphitic carbon in soft and in drawn steel*—Continued.

[S, annealed from red heat, with very slow cooling (commercial). SA, heated to redness and cooled in air. GH, glass-hard. An, annealed at 500°. Dr, fresh drawn, usually from diameter $= 2\rho = 0{\cdot}13^{cm}$ to $2\rho = 0{\cdot}08^{cm}$.]

Before drawing.			Before dissolving.		M	$m \times 10^3$	$\frac{m}{M} \times 10^3$	No.
Original condition.	Final condition.	$2\rho \times 10^3$	Condition.	$2\rho \times 10^3$				
S	SA	130	SA	130	3·25	24·2	7·4	17
S	SA	130	Dr	80	2·94	15·7	5·3	18
S	S	130	S	130	3·28	24·6	7·5	19
S	S	130	Dr	80	3·07	19·5	6·3	20
S	S	130	S	130	3·26	23·0	7·0	21
S	S	130	Dr	80	3·08	19·5	6·3	22
S	S	140	S	140	3·95	28·6	7·2	23
S	S	140	Dr	80	3·34	29·0	8·7	24
S	S	140	S	140	4·00	28·6	7·1	25
S	S	140	Dr	80	3·48	35·3	10·1	26
S*	S	140	S	140	4·16	4·6	1·1	27
S*	S	140	Dr	80	3·05	5·8	1·9	28
S	S	140	S	140	4·36	29·7	6·8	29
S	S	140	Dr	80	8·54	21·8	6·1	30
GH	SA	130	SA	130	3·23	16·6	5·1	31
GH	SA	130	Dr	90	2·82	20·7	7·3	32
GH	SA	130	SA	130	3·25	16·7	5·1	33
GH	SA	130	Dr	90	2·61	15·4	5·9	34
(†)			S	120	2·29	14·7	6·4	35
(‡)			S	120	2·25	13·6	6·0	37
(†)			S	120	2·27	14·6	6·4	36
(‡)			S	120	2·22	11·5	5·2	38
	HCl	29%	S	120	3·10	25·3	8·1	39
	HCl	22%	S	120	3·25	24·2	7·4	40
	HCl	15%	S	120	3·13	27·0	8·6	41
	HCl (conc)	38%	S	120	3·25	32·6	10·0	42
Beaker	HCl	25%	S	130	3·14	24·3	7·7	43
Erl. flask, etc	HCl	25%	S	130	3·21	9·9	3·1	44
Erl. flask, etc	HCl	12%	S	130	3.13	23·6	7·5	45
Beaker, boiling	HCl	25%	S	130	3·20	1·5	0·5	46
Beaker, boiling	HCl	10%	S	130	....	0·0	0·0	46*a*
S	S	130	S	80	2·37	15·4	6·5	§47
S	S	130	Dr	80	2·39	16·8	7·0	‖48
Dissolved in a beaker under identical conditions of concentration and temperature.								
	S	130	S	130	2·59	18·3	7·1	49
	S	130	Dr	80	2·58	19·6	7·6	50
	S	130	S	130	2·48	22·9	9·2	51
	S	130	Dr	80	2·48	17.2	6·9	52

* Dissolved in boiling acid, sp. gr., 1·15, 30% HCL.

† Dissolved in cold acid, sp. gr., 1·15, 30% HCL.

‡ Dissolved in dilute cold acid, sp. gr., 1·07, 15% HCL.

§ Dissolved down.

‖ Drawn down.

TABLE 10.—*Graphitic carbon in soft and drawn steel*—Continued.

[S, annealed from red heat, with very slow cooling (commercial). SA, heated to redness and cooled in air. GH, glass-hard. An, annealed at 500°. Dr, fresh drawn, usually from diameter $= 2\rho = 0{\cdot}13^{\mathrm{cm}}$ to $2\rho = 0{\cdot}08^{\mathrm{cm}}$.]

Dissolved under identical conditions in Erlenmeyer flask with Bunsen valve. Acid 1·13 at 24°. 60cc taken per 1 gr. iron.

Before drawing.			Before dissolving.		M	$m\times10^3$	$\frac{m}{M}\times10^3$	No.
Original condition.	Final condition.	$2\rho\times10^3$	Condition.	$2\rho\times10^3$				
	S	130	S	130	3·16	12·5	3·9	53
	S	130	Dr	80	1·77	8·2	4·6	54
	S	130	S	130	3·19	12·3	3·8	55
	S	130	Dr	80	2·21	6·9	3·1	56
GH	SA	130	SA	130	3·03	11·8	3·9	57
GH	SA	130	Dr	80	2·51	9·1	3·6	58
GH	SA	130	SA	130	3·19	11·3	3·5	59
GH	SA	130	Dr	80	2·82	6·6	2·3	60
	S	130	S	130	5·77	20·1	3·5	61
	S	130	Dr	80	5·46	6·3	1·1	62
	S	80	GH	80	4·35	....	0·0	63
	S	80	An. 450	80	3·50	4·2	1·2	64

DISCUSSION.

20. *Inconsistency of the results.*—To obtain a comprehensive survey over this large number of data, it is expedient to lay them down graphically. This can be done clearly by erecting perpendiculars equidistant, on the same base for each of the states S, SA, GHSA, Dr, Dr, SA, etc., and laying off the divers carburation data *m* along the vertical lines. Points belonging to the halves or other parts of the same wire are then connected by a line with an arrow indicating the direction of the operation. Thus, S ⟶ Dr would denote that one-half of the originally soft rod was drawn down, the remainder being left in the soft state.

It is well to commence with the rods Nos. 1 to 22, all of these being of the same kind of steel (diameter 130^{cm}). It will be seen that the drawn wires here lie within a relatively narrow zone, whereas the soft wires are widely scattered. The diagram is such as to suggest very pointedly that the operation of drawing steel either precipitates or dissolves carbon according as the amount of free carbon in soft steel is less or greater than the quantity needful for the drawn state. Fortunately, however, I was induced to suspect an error in these data notwithstanding their general consistency and number; for the behavior of the couple Nos. 15 and 16, for instance, is anomalous. I may remark in passing that Nos. 7 and 8 showed the marked difference of rate of solution already referred to in § 18 Nos. 11, 12, and due to the resolution of carbon produced by annealing a thoroughly soft wire in air, etc. Nevertheless so remarkable a result was not to be rashly enunciated, and I therefore resolved to continue the experiments with steel of another kind. Rods 23 to 30 were tested. The results here obtained were such as wholly to vitiate the inferences drawn from the first lot. At least the drawn samples now lie far apart, and away from the earlier drawn group, whereas the soft rods are more nearly identical. Hence it began to appear that the data in hand had no discernible meaning at all; that the differences of the carburation positions of the soft and drawn wire were the result of flaws in the method of chemical treatment. These adverse views are substantiated by Nos. 27 and 28, which were boiled during solution. The result is a sacrifice of all but one-fifth or less of the free carbon found after dissolving in cold acid. A few additional experiments, Nos. 31 to 34, made with the first steel wire, corroborate the remarks made relative to the deep-seated insufficiency of the method.

21. *Errors of the method.*—Having been obliged to come to these unfavorable conclusions I thought it desirable, in view of the importance of the results to be reached, to make some attempt in perfecting the method. The experiments 35 to 52 are made chiefly with this end in view. The sources of error are unfortunately so complex as to make the interpretation a problem of almost insuperable difficulty. There are at least six such sources to be considered, viz, temperature; the concentration of the solvent acid; the effect of solution in air, and in hydrogen; the rate of solution; the variations of structural density of the wire, etc.

22. *Temperature.*—Nos. 27 and 28, already given, and Nos. 46 and 46*a* show that at 100° nearly all the free carbon is removed during solution; and that this is the case moreover for acids of any reasonable strength (HCl, 12 % to 25 %). Hence, since the amount of free carbon obtained rapidly diminishes (cæt. par.) with increasing temperature, it follows that data for two samples are not comparable unless the temperature has remained constant throughout the whole interval of solution for each. Particularly does this apply in case of different weights.

23. *Concentration of acid.*—The strength of acid used is an item of even greater importance. This is shown by Nos. 35 to 45. In the first group of experiments, Nos. 35 to 38, the effect of concentration in increasing the amount of free carbon is already apparent. Experiments 39, 40, 41, 42, however, show this more convincingly. In case of concentrated acid (No. 42) nearly all the carbon in steel is precipitated during solution. In all such experiments, however, the time of solution is an essential consideration. I do not refer so much to the rate of solution as to the time of exposure of the liquid to air or other gases. In the present instance, No. 41, which dissolved very slowly in the dilute acid, has an exceptionally high position. To some extent the same influence may be present in No. 42, which also dissolved very slowly under the opposite conditions of very strong acid.

24. *Solution in air and in hydrogen.*—The large differences obtained

for these two cases are shown in Nos. 43 to 45, and in most of the experiments Nos. 49 to 62. The results here obtained are the most important of the present section, inasmuch as they indicate the probable nature of the error of the method and the steps necessary to perfect it. Comparing Nos. 43 and 44, it appears that the solution in hydrogen, i. e., in an Erlenmeyer flask provided with a Bunsen valve, is accompanied with a precipitation of less than one-half as much carbon as separates out under the ordinary conditions of solution in a covered beaker. If the acid be very dilute (No. 45) so that solution takes a very long time, then the effect of the Bunsen valve is nil, because it is not sufficiently tight. It follows from these data that the solution of soft steel is not generally a simple phenomenon; that an *oxidizable* hydrocarbon or similar compound escapes, which in presence of air or available oxygen deposits carbon by secondary decomposition. This inference is conclusively substantiated by the beaker series, Nos. 49 to 52, as compared with the flask series (Bunsen valve), Nos. 53 to 56. When solution takes place in a covered beaker, the carbon precipitate, besides being in larger amount, is different in character from the flask precipitate. The latter is heavy and graphitic; the former contain as very light suspended admixture, which it is difficult to wash down in the Gooch crucible.

25. *Rate of solution.*—Whether the rate of solution has any direct influence on the carbon deposited, I am unable to affirm with certainty. If it does, the effect is probably small; for instance, solution in concentrated HCl (No. 42) takes place relatively slowly, as does also solution in dilute acid (41). But the large amount of carbon found is probably due to atmospheric influence. Nevertheless, in view of the large thermal effect already pointed out, it can not be asserted that the rate of solution is a negligible factor.

26. *Structural density.*—In experiments Nos. 47 and 48 one sample was drawn down and the other diminished in diameter by solution, whereupon both were identically dissolved for analysis. There is no difference in free carbon discernible. Inasmuch, however, as the drawn strain is characterized by superficial condensation accompanied by core dilatation, I was induced to ascribe the differences in the values of *m* for rods Nos. 57 to 62 to some such cause; for here the experiments were made in a way to take advantage of all refinements of research. Yet the low value of No. 62 (corroborated) defies explanation. Had the precipitate been too large it might have been ascribable to an imperfect valve.

27. *Summary.*—Summarizing the above, I conclude that such carburation differences as appear in the above data are to be looked upon as the result of secondary decomposition. In the case of soft steel the solution in HCl produces an unstable carbide which, under the influence of an oxidizing agency, splits up with a deposition of carbon. The precipitate found in such cases is no indication at all of the carbon actually

free in steel. So far as the above results go, the effect of mechanical strain on the carburation of steel is not demonstrable; at least all molecular disintegration superinduced by mechanical means is negligible in comparison with the present errors of the method for estimating free carbon. It might be inferred that the qualitative difference in the carburations of glass-hard and of soft steel is also to be suspected. In this case, however, sharp distinction may be made as follows: In glass-hard steel it is impossible by any rational method of treatment to obtain precipitation of free carbon out of the solution. In soft steel it is equally impossible by the same rational method of treatment to dissolve without a free-carbon deposit. For intermediate tempers proportionate amounts are deposited (cf. Nos. 63 and 64, which close the analyses).

Finally, to distinguish between the different kinds of carburation empirically, two methods suggest themselves: Solution may be made either in a current of hydrogen in hermetically-closed vessels, under identical conditions of concentration (grammes HCl, per gramme water, per gramme steel), and of temperature, etc., for all wires; or else in a current of oxygen under the same identical conditions. In the former case presumably only the free carbon in the steel is actually deposited. In the latter case (oxidation) the free carbon is definitely incremented by the deposition obtained from the oxidizable unstable carbide.

I took steps toward testing the first of these methods (solution in a current of hydrogen), but have thus far been prevented from pushing the question decisively to an issue.

28. *Osmond's α and β iron.*—If the difference between steel hardened mechanically and the same steel soft is due to Osmond's α and β iron (cf. § 5), then the possibility of molecular change due to the mechanical treatment is beyond the province of the present method. It is well to bear this in mind. Carbon under certain conditions may be favorable to the stability of β iron, but it is not essential to its existence beyond a certain relative quantity. In view of these considerations the experiments of the next chapter are more pertinent to the subject of inquiry.

CHAPTER IV.

THE EFFECT OF STRAIN ON THE RATE OF SOLUTION OF STEEL.

INTRODUCTORY.

29. The difficulties encountered in the preceding section, in which the effect of strain on carburation is directly put to test, suggested a possible solution by indirect methods. It is well known that the effect of mechanical treatment, for instance, of rolling, drawing, etc., is apt to show itself in the structure of the metal when acted on by acids. The fiber of iron may thus be clearly exhibited; and even in cases of galvanic solution the surface often becomes furrowed and marked in a way indicative of definite structure. It appears, therefore, that some parts of the metal are more electropositive than others; and it does not seem improbable that homogeneous and strained metal may be distinguished by studying their respective rates of solution under given conditions.

METHOD.

30. Solution experiments of this kind are given in the following tables. The method of experiment is again simple. The weighed rods of known length are placed in a small tray made of narrow strips of hard rubber. Thus they can all be submerged or withdrawn from the acid at the same time. Some care was necessary as regards drying the samples before weighing. Having taken them out of the solution on the tray (this was # shaped, with the wires placed across either set of parallel bars or rubber strips are placed edge upward), the wires were submerged in water and then dried in an air bath at 100°. The bars of the tray were notched so as to avoid displacement of the wires. As they could be carried together, it was not necessary to touch them except with the forceps before weighing. This structure of the tray, moreover, is such as to allow free circulation of acid. The essential data to be noted are the temperatures of the acid and the weight and length of each rod before and after dipping. From this the radius for each case may be calculated. Two series of experiments must be made for each group of steel rods. It is first necessary to find the consecutive solution data in case of *homogeneous* wire gradually decreasing in thickness; with these data the corresponding results for wire *drawn down* from the original homogeneous wire may then be compared.

TABLES.

31. In Table 11 I give the results for three identical, nearly homogeneous steel wires, about 5^{cm} long and originally ·127^{cm} thick, submerged in dilute acid of a given kind, for consecutive intervals of time of one hour each. Here θ is the temperature of the acid; m the mass of the rod in grammes, r the radius, and Δr the consecutive decrement of radius due to solution. The progress of the experiment may be followed by consulting either M or r. Corrections are applied for the reduction of length due to solution.

In Table 12 data are given for drawn steel, the thickness of the individual wires varying between ·127^{cm} and ·084^{cm}. They are all drawn down from the same sample of soft steel, so that the larger thicknesses are soft, the thinner wires very resilient and brittle. All wires, Nos. 1 to 7, are submerged together; but variations of strength of acid, time, and temperature are the causes of differences of mass dissolved in successive solutions. From Table 11, however, the rates of solution for different thicknesses of homogeneous wire are known. Hence the behavior of the drawn wires during each solution can be tested. In Table 12, M', r', $\Delta r'$ denote the mass, radius, and variation of radius of the drawn wire, $\Delta r'$ being simply the difference between consecutive values of r before and after solution. Δr may therefore be interpolated from Table 11 by making the first term of $\Delta r'$ and Δr identical. The wires of each group are submerged and withdrawn in like manner. In passing from group to group, however, a change of acid is unavoidable.

TABLE 11.—*Solution of soft (S) steel, normal experiment.*

[Time, 1^h. $l=5^{cm}$. $\delta=7{\cdot}7$].

θ $M\times10^3$ $r\times10^3$ $\Delta r\times10^3$	θ $M\times10^3$ $r\times10^3$ $\Delta r\times10^3$	θ $M\times10^3$ $r\times10^3$ $\Delta r\times10^3$	θ $M\times10^3$ $r\times10^3$ $\Delta r\times10^3$	θ $M\times10^3$ $r\times10^3$ $\Delta r\times10^3$	θ $M\times10^3$ $r\times10^3$ $\Delta r\times10^3$	θ $M\times10^3$ $r\times10^3$ $\Delta r\times10^3$	θ $M\times10^3$ $r\times10^3$ $\Delta r\times10^3$	θ $M\times10^3$ $r\times10^3$ $\Delta r\times10^3$	θ $M\times10^3$ $r\times10^3$ $\Delta r\times10^3$	θ $M\times10^3$ $r\times10^3$ $\Delta r\times10^3$	θ $M\times10^3$ $r\times10^3$ $\Delta r\times10^3$
32·4	32·4	32·4	31·6	31·6	31·6	33·3	33·3	33·3	31·5	31·5	31·5
495	496	497	351	354	355	207	209	211	90	93	93
63·8	64·0	64·0	53·8	54·0	54·2	41·3	41·5	41·7	27·2	27·7	27·7
0	0	0	2·8	2·7	2·6	3·5	3·4	3·3	3·0	2·9	3·1
32·3	32·3	33·3	32·5	32·5	32·5	33·3	33·3	33·3	31·7	31·7	31·7
464	466	467	314	316	317	171	174	175	65	68	68
61·9	62·0	62·1	50·8	51·0	51·1	37·6	38·0	38·1	23·1	23·6	23
1·9	2·0	1·9	3·0	3·0	3·1	3·7	3·5	3·6	4·1	4·1	4·1
32·3	32·3	32·3	32·5	32·5	32·5	32·8	32·8	32·8	32·0	32·0	32·0
426	427	428	280	281	282	137	140	142	41	43	44
59·3	59·4	59·4	48·0	48·1	48·2	33·7	34·1	34·3	18·3	18·8	19·0
2·6	2·6	2·7	2·8	2·9	2·9	3·9	3·9	3·8	4·8	4·8	4·6
32·0	32·0	32·0	33·0	33·0	33·0	31·5	31·5	31·5	32·0	32·0	32·0
389	390	391	243	244	245	111	114	115	21	23	23
56·6	56·7	56·8	44·8	44·9	45·0	30·2	30·6	30·8	13·1	13·7	13·7
2·7	2·7	2·6	3·2	3·2	3·2	3·5	3·5	3·5	5·2	5·1	5·3

TABLE 12.—*Solution of drawn steel, originally S.*

[$l=4{\cdot}5^{\mathrm{cm}}$. $\delta=7{\cdot}7$.]

$M'\times10^3$ $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$	$M'\times10^3$ $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$	$M'\times10^3$ $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$	$M'\times10^3$ $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$	$M'\times10^3$ $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$	$M'\times10^3$ $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$	$M'\times10^3$ $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$
No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.
441	413	359	309	248	203	193
63·5	61·5	57·3	53·2	47·5	43·3	42·0
....	....	....	....	....	....	....
....	....	....	....	....	....	....
411	376	324	267	218	176	167
61·4	58·6	54·3	49·5	44·7	40·3	39·2
2·1	2·9	3·0	3·7	2·8	3·0	2·8
2·1	2·2	2·3	2·3	2.5	2·7	2·7
384	348	288	233	184	148	137
59·3	56·4	51·4	46·2	41·1	36·7	35·5
2·1	2·2	2·9	3·3	3·6	3·6	3·7
2·1	2·1	2·2	2·4	2·5	2·7	2·7
367	325	264	204	155	117	106
58·0	54·5	49·1	43·4	37·7	32·7	31·1
1·3	1·9	2·3	2·8	3·4	4·0	4·4
1·3	1·3	1·4	1·5	1·6	1·7	1·8
337	292	229	166	119	79	66
55·4	51·7	45·8	39·1	33·0	26·9	24·6
2·6	2·8	3·3	4·3	4·7	5·8	6·5
2·6	2·7	2·9	3·2	3·5	3·7	4·0
313	264	198	136	94	53	37
53·4	49·1	42·6	35·4	28·9	22·1	18·5
2·0	2·6	3·2	3·7	4·1	3·9	6·1
2·0	2·1	2·3	2·5	2·8	3·1	3·3
286	237	170	109	63	24	13
51·2	46·6	39·5	31·7	23·9	15·0	10·9
2·2	2·5	3·1	3·7	5·0	7·1	7·6
2·2	2·3	2·5	2·8	3·3	3·8	(4·3)
238	185	113	69	31		
46·7	41·2	32·1	25·2	16·7		
4·5	5·4	7·4	6·5	7·2		
4·5	4·8	5·9	6·0	7·2		
197	144	90	41	6		
42·5	36·5	28·7	19·5	7·5		
4·2	4·7	3·4	5·7	9.2		
4·2	4·6	5·3	6·3			
130	84	38	2			
34·5	27·8	18·6	4·7			
8·0	8·7	10·9	2·8			
8·0	8·9	10·3				
98	56	12				
30·0	22·7	10·5				
4·5	5·1	8·1				
4·5	5·1	6·5				
67	25					
24·8	15·4					
5·2	7·3					
5·2	6·8					

Tables 13, 14, 15 and 16 are constructed on the same plan as Tables 11 and 12. The steel wires, however, are of different temper. Table 3 contains the normal experiments, the rods being submerged in hydrochloric acid of a given strength throughout during successive intervals of two hours each. The rods are about 5$^{\text{cm}}$ long, and Nos. 1, 2, 3 are annealed at red heat in air from the soft state; Nos. 4, 5, 6, annealed at red heat in air from the glass-hard state; No. 7 is glass-hard. θ, M, r, etc., have the signification already given. In Table 14 five soft rods, annealed at red heat in air, are tested. M', r', $\Delta r'$ are their solution data. Δr is interpolated from Table 13 by making the first term of Δr and $\Delta r'$ identical. In Table 15 six glass-hard rods, annealed at red heat in air, are tested. Notation as before. Abbreviations which refer to temper and hardness are given in § 19 above.

TABLE 13.—*Solution of soft (S A) steel, normal experiment.*

[$l = 5^{\text{cm}}$. $\delta = 7{\cdot}7$.]

S-S A.			G H-S A.			G H.
θ M $r\times10^3$ $\Delta r\times10^3$.	θ M $r\times10^3$ $\Delta r\times10^3$.	θ M $r\times10^3$ $\Delta r\times10^3$.	θ M $r\times10^3$ $\Delta r\times10^3$.	θ M $r\times10^3$ $\Delta r\times10^3$.	θ M $r\times10^3$ $\Delta r\times10^3$.	θ M $r\times10^3$ $\Delta r\times10^3$.
No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.
....	....	....	....	....	....	....
·489	·487	·486	·492	·495	·491	·489
63·5	63·4	63·2	63·7	63·8	63·5	63·5
....	....	....	....	....	....	....
32·4	32·4	32·4	32·4	32·4	32·4	32·4
·455	·452	·452	·461	·462	·461	·467
61·2	61·1	61·1	61·7	61·7	61·7	62·1
2·3	2·3	2·1	2·0	2·1	1·8	1·4
32·4	32·4	32·4	32·4	32·4	32·4	32·4
·415	·412	·413	·425	·425	·426	·441
58·5	58·3	58·3	59·3	59·3	59·3	60·3
2·7	2·8	2·8	2·4	2·4	2·4	1·8
28·7	28·7	28·7	28·7	28·7	28·7	28·7
·387	·383	·385	·398	·396	·400	·423
56·5	56·2	56·3	57·2	57·2	57·5	59·1
2·0	2·1	2·0	2·1	2·1	1·8	1·2
29·4	29·4	29·4	29·4	29·4	29·4	29·4
·358	·354	·356	·372	·369	·374	·404
54·3	54·0	54·1	55·4	55·1	55·5	57·6
2·2	2·2	2·2	1·8	2·1	2·0	1·5
29·3	29·3	29·3	29·3	29·3	29·3	29·3
·328	·325	·327	·345	·341	·348	·384
52·0	51·8	52·0	53·4	53·0	53·6	56·2
2·3	2·2	2·1	2·0	2·1	1·9	1·4
	29·5	29·5	29·5	29·5	29·5	29·5
	·296	·299	·318	·313	·320	·363
	49·5	50·3	51·3	50·8	51·4	54.8
	2·3	1·7	2·1	2·2	2·2	1·4

TABLE 13.—*Solution of soft (S A) steel, normal experiment*—Continued.

[$l=5^{cm}$. $\delta=7{\cdot}7$.]

S-S A.			G H-S A.			G H.
θ M $r\times10^3$ $\Delta r\times10^3$.	θ M $r\times10^3$ $\Delta r\times10^3$	θ M $r\times10^3$ $\Delta r\times10^3$.	θ M $r\times10^3$ $\Delta r\times10^3$.	θ M $r\times10^3$ $\Delta r\times10^3$.	θ M $r\times10^3$ $\Delta r\times10^3$.	θ M $r\times10^3$ $\Delta r\times10^3$.
No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No, 7.
	29·5	29·5	29·5	29·5	29·5	29·5
	·271	·276	·293	·287	·297	·345
	47·3	47·7	49·2	48·7	49·6	53·3
	2·2	2·6	2·1	2·1	1·8	1·5
	30·0	30·0	30·0	30·0	30·0	30·0
	·241	·245	·269	·261	·273	·326
	44·7	45·0	47·0	46·4	47.5	51·9
	2·6	2·7	2·2	2·3	2·1	1·4
	30·0	30·0	30·0	30·0	30·0	30·0
	·213	·218	·241	·233	·247	·306
	41·8	42·4	44·5	43·7	45·1	50·2
	2·9	2·6	2·5	2·7	2·4	1·7
	30·0	30·0	30·0	30·0	30·0	30·0
	·188	·193	·218	·208	·223	·287
	39·4	39·9	42·4	41·4	42·9	48·6
	2·4	2·5	2·1	2·3	2·2	1·6
	30·0	30·0	30·0	30·0	30·0	30·0
	·170	·174	·200	·189	·205	·271
	37·5	37·9	40·7	39·5	41·2	47·3
	1·9	2·0	1·7	1·9	1·7	1·3
	31·5	31·5	31·5	31·5	31·5	31·5
	·146	·152	·177	·164	·183	·250
	34·7	35·5	38·2	36·7	38·9	45·4
	2·8	2·4	2·5	2·8	2·3	1·9
	29·0	29·0	29·0	29·0	29·0	29·0
	·124	·129	·156	·144	·162	·232
	31·9	33·1	35·9	34·4	36·6	43·8
	2·8	2·4	2·3	2·3	2·3	1·6
	28·3	28·3	28·3	28·3	28·3	28·3
	·107	·112	·138	·124	·144	·217
	29·6	30·5	33·7	32·0	34·6	42·3
	2·3	2·6	2·2	2·4	2·0	1·5
	27·6	27·6	27·6	27·6	27·6	27·6
	.089	·094	·120	·106	·127	·202
	27·0	27·8	31·5	29·5	32·3	40·8
	2·6	2·7	2·2	2·5	2·3	1·5
	27·0	27·0	27·0	27·0	27·0	27·0
	·073	·078	·104	·089	·110	·187
	24·5	25·4	29·2	27·1	30·1	39·2
	2·5	2·4	2·3	2·4	2·2	1·6

TABLE 14.—*Solution of drawn steel, originally S, changed to SA.*

[$l=4.0^{cm}$. $\delta=7.7$.]

M' $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$	M' $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$	M' $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$	M' $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$	M' $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$
No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
·390	·340	·264	·212	·167
63·4	59·1	52·1	46·8	41·5
·381	·329	·251	·201	·153
62·7	58·2	50·8	45·6	39·8
0·7	0·9	1.3	1·2	1·7
0·7	0·7	0·7	0·8	0·8
·372	·321	·242	·188	·143
61·9	57·5	50·0	44·3	38·5
0·8	0·7	0·8	1·3	1·3
0·8	0·8	0·8	0·9	0·9
·368	·316	·235	·180	·134
61·3	57·0	49·2	43·1	37·1
0·5	0·5	0·8	1·2	1·4
0·5	0·5	0·5	0·6	0·6
·359	·307	·225	·169	·121
60.8	56·3	48·2	41·8	35·3
0·5	0·7	1.0	1·3	1·8
0·5	0·5	0·5	0·6	0·6
·352	·301	·215	·159	·107
60·3	55·7	47.2	40·7	33·4
0·5	0·6	1·0	1.1	1·9
0·5	0·5	0.5	0·6	0·6
·346	·293	·205	·148	·094
59·8	54·9	46·0	39·1	31·2
0·5	0·8	1·2	1·6	2·2
0·5	0·5	0.6	0·6	0·6
·330	·271	·183	·124	·068
58·4	52·8	43·3	35·8	26·6
1·4	2·1	2·7	3·3	4·6
1·4	1·4	1·5	1·6	1·7
·312	·259	·162	·102	·047
56·9	51·6	41·3	32·8	22·3
1·5	1·2	2·0	3·0	4·3
1·5	1·6	1·6	1·7	1·8
·277	·223	·129	·066	·014
53·4	47.9	36.5	26·1	11.8
3·5	3·7	4.8	6.7	10·5
3·5	3·6	3·8	4·1	
·264	·206	·110	·048	
52·0	46·2	33·7	22·5	
1·4	1·7	2·8	3·6	
1·4	1·4	1·6	1·7	

TABLE 14.—*Solution of drawn steel, originally S, changed to SA*—Continued.

[$l=4.0^{\mathrm{cm}}$. $\delta=7.7$.]

M' $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$	M' $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$	M' $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$	M' $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times103$	M' $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$
No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
·246	·188	·093	·031	
50·4	44.1	31·1	18·0	
1·6	2.1	2·6	4·5	
1·6	1·7	1·8	1·9	
·230	·171	·075	·016	
48·7	42·2	27·9	13·3	
1·7	1·9	3.2	4·7	
1·7	1·8	1·9		
·214	·156	·058		
46·9	40·2	25·0		
1·8	2·0	2·9		
1·8	1·9	2.1		
·199	·140	·043		
45·3	38·1	21·4		
1·6	2·1	3.6		
1·6	1·6	1·8		
·176	·117	.026		
42·6	34·6	16·5		
2·7	3·5	4·9		
2·7	2·8			
·143	·086			
38·5	29·8			
4·1	4·8			
4·1	4.3			
·129	·072			
36·5	27·3			
2·0	2·5			
2·0	2·1			

TABLE 15.—*Solution of drawn steel, originally GH, changed to SA.*

[l=3·8cm to 4·0cm. δ=7·7.]

M' $r' \times 10^3$ $\Delta r' \times 10^3$ $\Delta r \times 10^3$	M' $r' \times 10^3$ $\Delta r' \times 10^3$ $\Delta r \times 10^3$	M' $r' \times 10^3$ $\Delta r' \times 10^3$ $\Delta r \times 10^3$	M' $r' \times 10^3$ $\Delta r' \times 10^3$ $\Delta r \times 10^3$	M' $r' \times 10^3$ $\Delta r' \times 10^3$ $\Delta r \times 10^3$	M' $r' \times 10^3$ $\Delta r' \times 10^3$ $\Delta r \times 10^3$
No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.
·393	·321	·272	·229	·186	....
63·8	59·0	54·3	49·9	44·9	....
....	....	....	....	....	....
....	....	....	....	....	....
·382	·311	·261	·217	·176	·151
62·8	58·7	53·2	48·5	43·7	40·5
1·0	1·3	1·1	1·4	1·2	....
1·0	1·0	1·1	1·1	1·2	....
·375	·305	·254	·209	·168	·143
62·1	57·4	52·4	47·8	42·9	39·8
0·7	1·3	0·8	0·7	0·8	0·7
0·7	0·7	0·7	0·7	0·8	0·8
·371	·303	·249	·204	·164	·139
61·8	57·3	52·0	47·2	42·3	39·4
0·3	0·1	0·4	0·6	0·6	0·3
0·3	0·3	0·3	0·3	0·3	0·3
·363	·294	·242	·195	·154	·137
61·1	56·5	51·2	46·0	40·9	38·6
0·7	0·8	0·8	1·2	1·4	0·8
0·7	0·7	0·7	0·7	0·8	0·8
·356	·288	·235	·187	·148	·126
60·5	55·9	50·5	45·1	40·1	37·0
0·6	0·6	0·7	0·9	0·8	1·6
0·6	0·6	0·6	0·7	0·7	0·7
·350	·282	·229	·180	·139	·119
60·1	55·2	49·9	44·2	38·8	36·0
0·4	0·7	0·6	0·9	1·3	1·0
0·4	0·4	0·4	0·5	0·5	0·5
·329	·260	·207	·156	·116	·094
58·3	53·1	47·5	41·1	35·3	32·1
1·8	2·1	2·4	3·1	3·5	3·9
1.8	1·8	1·9	2·0	2·0	2·0
·311	·244	·188	·136	·096	·072
56·7	51·4	45·3	38·4	32·2	28·0
1·6	1·7	2·2	2·7	3·1	4·1
1·6	1·7	1·8	1·8	1·9	2·7
·277	·214	·156	·102	·055	·027
53·4	48·3	41·2	33·3	25·4	18·3
3·3	3·1	4·1	5·1	6·8	9·7
3·3	3·4	3·6	3·7	4·0	4·0
·261	·199	·138	·081	·038	·014
51·9	46·5	38·7	29·6	21·3	12·7
1·5	1·8	2·5	3·7	4·1	5·6
1·5	1·5	1·6	1·7	1·8	

TABLE 15.—*Solution of drawn steel, originally GH, changed to SA.*—Continued.

[$l=3{\cdot}8^{\text{cm}}$ to $4{\cdot}0^{\text{cm}}$. $\delta=7{\cdot}7$.)

M' $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$	M' $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$	M' $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$	M' $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$	M' $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$	M' $r'\times10^3$ $\Delta r'\times10^3$ $\Delta r\times10^3$
No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.
·244	·183	·121	·065	·021	
50·1	44·6	36·5	27·4	16·7	
1·8	1·9	2·2	2·2	4·6	
1·8	1·9	2·0	2·1		
·229	·167	·105	·049	·008	
48·6	42·5	33·7	23·3	11·8	
1·5	2·1	2·8	4·1	4·9	
1·5	1·6	1·7	1·8		
·213	·150	·090	·034		
46·9	40·3	31·4	19·4		
1·7	2·2	2·3	3·9		
1·7	1·8	1·9	2·0		
·197	·136	·074	·021		
45·1	38·5	28·5	15·4		
1·8	1·8	2·9	4·0		
1·8	1·8	2·0			
·174	·114	·053			
42·4	35·2	24·0			
2·7	3·3	4·5			
2·7	2·8	3·0			
·140	·085	·028			
38·1	30·3	18.8			
4·3	4·9	5·2			
4·3	4·5				

Finally, in table 16, solution comparisons are made between glass-hard and soft wires, in the way indicated for the preceding tables. Rods Nos. 1 and 2 are glass-hard; Nos. 3 and 4 soft; Nos. 5 and 6 annealed at low red heat in air; No. 7 annealed at very high red heat in air. The time of submergence was 3 hours.

TABLE 16.—*Solution of steel, GH, S, SA.*

[$l = 5^{cm}$. $\Delta = 7 \cdot 7$.]

GH.		S.		S-SA.		SA.	θ
No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.	
$M \times 10^3$ $r \times 10^3$ $\Delta r \times 10^3$	$M \times 10^3$ $r \times 10^3$ $\Delta r \times 10^3$	$M \times 10^3$ $r \times 10^3$ $\Delta r \times 10^3$	$M \times 10^3$ $r \times 10^3$ $\Delta r \times 10^3$	$M \times 10^3$ $r \times 10^3$ $\Delta r \times 10^3$	$M \times 10^3$ $r \times 10^3$ $\Delta r \times 10^3$	$M \times 10^3$ $r \times 10^3$ $\Delta r \times 10^3$	
487 63·4	201 40·7	489 63·5	205 41·1	487 63·4	199 40·5	487 63·4	
483 63·1 0·3	199 40·5 0·2	445 61·2 2·3	189 39·8 1·3	477 62·7 0·7	195 40·1 0·4	481 63·0 0·4	28
477 62·7 0·4	196 40·2 0·3	387 57·7 3·5	167 37·8 2·0	465 62·1 0·6	191 39·8 0·3	475 62·5 0·5	28
469 62·2 0·5	193 39·9 0·3	324 53·3 4·4	144 35·4 2·4	453 61·4 0·7	186 39·3 0·5	469 62·2 0·3	
462 61·7 0·5	189 39·4 0·5	259 48·2 5·1	120 32·6 2·8	439 60·4 1·0	181 38·7 0·6	462 61·7 0·5	
455 61·2 0·5	186 39·2 0·2	201 42·8 5·4	99 29·8 2·8	424 59·4 1·0	176 38·3 0·4	455 61·2 0·5	
448 60·8 0·4	183 38·8 0·4	146 36·9 5·9	78 26·8 3·0	412 58·6 0·8	170 37·7 0·6	447 60·7 0·5	
442 60·4 0·4	180 38·5 0·3	102 31·0 5·9	61 23·8 3·0	400 57·8 0·8	165 37·1 0·6	442 60·4 0·3	
436 60·0 0·4	177 38·2 0·3	....	45 20·5 3·3	387 57·0 0·8	161 36·7 0·4	435 59·8 0·6	

DISCUSSION.

32. *Incidental errors.*—I may state at the outset that secondary errors, such, for instance, as might be ascribed to passivity of steel, are largely avoided. Care was taken to rub the rod with platinum at the beginning of each solution. Nevertheless, it is not impossible, when the rods were left to dry over night, at the close of a day's series of experiments, that some retardation during the first stages of solution on the succeeding day may be appreciable. A serious difficulty is encountered because of the unavoidable change of the room temperature during the successive solutions. In some instances I endeavored partially to avoid this by making the solution in the cellar underneath the laboratory. But even here the temperature is insufficiently constant for fine work.

33. *Effect of surface.*—As regards the plan of treating the above results, it appears probable that the masses dissolved in case of a given sample and given solvent, must be simply a function of radius and time (correction being made, of course, for loss at the ends). If the rate of solution be denoted by ρ, its value at the radius r must be

$$\rho_r = -\delta\cdot 2\pi r dr/2\pi r dt$$

where δ is the density of the sample and dt the elementary time of solution. ρ therefore is the mass dissolved under the given condition of form and solvents per unit of surface, per unit of time. Thus it appears that the mean rate during the time t will be

$$(\int\rho_r dt)/t \text{ or } -(\delta/t)/\int dr,$$

each taken between corresponding limits. In other words the mean rate

$$\rho = \frac{1}{t}\int_{t_1}^{t_2}\rho_r dt = \frac{\delta}{t}(r_2 - r_1)$$

where $t_2 - t_1 = t$. If therefore t be chosen constant, rates of solution are to each other as

$$\frac{\rho'}{\rho} = \frac{r_2' - r_1'}{r_2 - r_1}.$$

It is, therefore, an apparently simple problem to deduce the relative mean rate directly from the differences of radii—time, figure, and chemical conditions remaining the same. But from the data of the above tables such simple relations do not at all appear. Indeed the corresponding differences of mass dissolved are very much more nearly constant than the corresponding differences of radii. In other words, in the case of cylindrical figures of small radius, the mass dissolved is nearly independent of radius; i. e., independent of the surface exposed to the action of acid. The conditions are such that fixed masses of solid are transferred by solution to the liquid state, and in proportion as radius diminishes the thickness of shell dissolved in given times rapidly increases.

34. *Effect of diffusion.*—Without doubt the underlying cause of this observation is a diffusion phenomenon. For instance, let c be the concentration at the surface of separation of solid and liquid, the radius being r. Then $c.2\pi r dr$ is the amount of salt dissolved in the first liquid shell. Now, when this salt dissolved is transferred by diffusion to a distance r' ($r' > r$), the concentration c' is necessarily smaller, for $c.2\pi r dr = c'2\pi r' dr'$, or $cr = c'r'$. It follows at once that the difference of concentration for a given value of dr increases at a rapid rate when the radius approaches zero. On the other hand the rate of transference of the solid material into the liquid state must depend on the rapidity with which c diminishes in the direction of r. Hence the rate of solution will increase in proportion as smaller thicknesses of wire are encountered, inasmuch as the conditions favorable for the transportation of the dissolved metal are enhanced. This follows more rigorously from Fick's law. Adapting Fourier's theory of heat conduction to questions involving diffusion, Fick[1] proposed $dc/dt=\varkappa d^2c/dx^2$, where c is the concentration and $\varkappa$ the diffusion constant. In other words, the time rate at which concentration progresses is proportional to the space rate of increase of the same quality. The truth of this fundamental assumption was afterwards rigorously tested by H. F. Weber.[2] Fick's equation, when $dc/dt=0$, or the diffusion has become stationary, referred to polar coordinates is $d^2(rc)/dr^2=0$. Since $c=0$ for $r=\infty$, this reduces to $cr=c'r'$.

The diffusion effect will necessarily be of smaller consequence when solution takes place at very low rates; for instance, in the case of glass-hard steel. It is also greatly modified, past recognition, perhaps, by the escape of gases from the body undergoing solution. In this way convective currents are set up accompanied by distributive effects very much more rapid than the diffusion phenomenon. A further disturbance is gravitational convection.

35. *Wires originally soft.*—Nevertheless, in discussing the above results, it is advisable to consider the relative consecutive value of ΔM for given comparable conditions of solution, quite as much as the relative values of Δr, or the consecutive rates. Inasmuch as there is a striking tendency toward constant values of ΔM independent of r, when r lies below a critical value, apparent in all my results, it is probable that a law characteristic of the solution of filimentary or small bodies is here expressed.

Turning first to Table 11, the following correlative values of $r=(r_2+r_1)\frac{1}{2}$; $\rho=r_2-r_1$ and $\Delta M=M_2-M_1$ are apparent. The variable ρ is identical with the rate, since the times and chemical conditions of solution are constant.

TABLE 17.—*Digest for originally soft wires.*

$r\times10^3=$	63	61	58	55	52	49	46	43	40	36	32	29	25	21	16
$\rho\times10^3=$	2·0	2·6	2·7	2·7	3·0	2·9	3·2	3·4	3·6	3·9	3·5	3·0	4·1	4·7	5·2
$\Delta M\times10^3=$	30	39	37	37	37	35	37	35	36	33	27	21	25	24	21

The salient property of these data is the rapid increase of rate encountered immediately after the superficial layer is dissolved off. After this ΔM is nearly constant between $r=.060^{\text{cm}}$ and $r=.040^{\text{cm}}$, whereupon it decreases rapidly. On the other hand ρ increases continually and at an accelerated rate. Irregularities of outline are doubtless

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[1] Fick: Pogg. Ann., xciv, p. 59, 1855; Phil. Mag. (4), x, p. 30, 1855.

[2] H. F. Weber: Phil. Mag. (5), viii, p. 523, 1879; Wied. Ann., vii, p. 469, 536, 1879.

the effect of temperature. The distortion is greatest in the curve for ΔM. With these data the seven drawn rods of Table 12 are to be compared. As before $2r' = r'_1 + r'_2$ and $\rho' = r'_2 - r'_1$ for each solution, and Table 11 furnishes values of ρ in case of the normal rod, for every value of r'. By making the first term of each series identical a corresponding series of $\Delta r = \rho$ is obtained. It is expedient to represent ρ and ρ' graphically as functions of r'. If this be done it appears that after the first shell is dissolved, the solution of drawn wire takes place at greater rates than the solution of homogeneous wire of the same radius. After dissolving seven shells the results show irregularities, easily accounted for inasmuch as the finer rods gradually become of irregular shape and fissured. Again the results for ΔM may be represented as a function of r', showing values, which as a rule, increase as r' decreases. From these data as a whole it follows that drawn steel is cæt. par. more easily soluble than homogeneous steel; again after the superficial layers are removed the rate of solution increases with the intensity of drawn strain or resilient properties of the wire.

36. *Wires annealed.*—Turning now to the results of Table 3, in which the normal data for wires softened in air and for a glass-hard wire are inserted, it is clear in the first place that as soon as the superficial layers are removed the rate of solution increases. This result corroborates Table 11. Apart from this, however, the variations of rate of solution and of the other data are here of a much smaller order than was the case for Table 11. ΔM decreases with radius at a somewhat more rapid rate than before, and hence $\rho' = \Delta r'$ now increases at a decidedly less rapid rate than in Table 11. This is shown in the following summary for wires softened in air (i. e., S–SA and GH–SA).

TABLE 18.—*Digest for wires annealed in air.*

$10^3 \times r = \ldots\ldots$	62	60	58	56	54	52	50	46	44	42	40	38	35	33	30	28
$10^3 \times \rho' = \ldots\ldots$	2·1	2·6	2·0	2·1	2·1	2·1	2·2	2·4	2·6	2·3	1·8	2·5	2·4	2·3	2·4	2·4
$10^3 \times \Delta M = \ldots$	33	38	27	27	28	29	19	27	28	24	18	23	22	17	17	17

It is also shown in the results for the glass-hard wire (G. H.), identically submerged.

TABLE 19.—*Digest for hard wires.*

$10^3 \times r = \ldots\ldots$	63	61	60	58	57	55	54	53	51	49	48	46	45	43	41	40
$10^3 \times \rho = \ldots\ldots$	1·4	1·8	1·2	1·5	1·4	1·4	1·5	1·4	1·7	1·6	1·3	1·9	1·6	1·5	1·5	1·6
$10^3 \Delta M = \ldots\ldots$	22	26	18	19	20	21	18	19	20	19	16	21	18	14	16	15

With these data the values of tables 14 and 15 are to be compared in a way already enunciated in case of tables 11 and 12. The data being constructed graphically, it again follows, almost without exception, that both in tables 14 and 15 the rates of solution of drawn wires are greater than the similarly circumstanced rates for homogeneous wires.

There also is a weight of evidence in favor of the result that solution increases with the degree of resilience, i. e., the intensity of the drawn strain. In other words, rate of solution increases as the (drawn) diameter of the wire of each group diminishes, supposing as above that the superficial layers of the wire have been removed. Finally, in Table 14, $\varDelta M$ also continually increases from larger to smaller diameters, for each group, until the diameter of the rod has been considerably reduced. In Table 15, however, this result is not so pronounced, and $\varDelta M$ remains nearly constant.

Summarizing the above results as a whole, it follows that the rate of solution of drawn steel is greater than the rate of the same homogeneous metal similarly circumstanced. After the superficial layers (probably dense low-carbon steel) have been removed, the rate of solution increases with the intensity of drawn strain. To a smaller and less definite extent this is true also of the masses dissolved in equal times, in cases of resilience of different intensities, other things remaining the same.

37. *Relation to Drowne's inferences.*—Table 16 finally has been drawn up to show the enormous difference of rate of solution between glass-hard and soft steels. Submergence being identical for all rods, it is curious in the first place to note the difference of rate of Nos. 3 and 4, both being very soft steel, as well as the high rates of solution of these two rods as compared with the others. The special feature of these experiments is the fact that rods annealed at red heat in air dissolve quite as slowly as rods quenched glass hard; and this is particularly the case when the rods are annealed at high-red heat, No. 7. This observation calls to mind the inference of Dr. Drowne[1], viz, that "there is a limited range of temperature probably near the point of solidification of the metal, within which the separation of carbon from iron takes place, and that the amount of carbon separated in any given instance is proportional to the time consumed by the pig iron in passing through the limited range of temperature." Now, as the rate of solution increases directly with the free carbon in steel, caet. par., the present data substantiate Dr. Drowne's reasoning.

38. *Summary.*—Perusing the above pages as a whole, they furnish evidence favoring the opinion that the effect of strain on metallic structure is a reconstruction of the metallic molecule; but since the rate of solution of the drawn metal is greater, it does not follow that the results so obtained are due to the presence of β iron in α iron, unless it be supposed that the negative character of the former relative to the positive quality of α iron increases the rate of solution by local electric action. The corrugated and deeply fissured appearance of the rods after the radius has been much reduced is in keeping with this view. Indeed, an exceedingly curious action, which I frequently observed, may be mentioned. It often happens that the solution at the

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[1] T. M. Drowne: Trans. Am. Inst. Mining Eng., III, 1874–'75, p. 41.

ends of the rod, instead of rounding off the corners, eats its way decidedly into the axis, so as to form a reentrant cone of some depth. Again, if there be periodic distributions of density from the surface inward, an inference which from earlier observations[1] with glass-hard rods does not seem improbable, the regularity of solution experiments would be disturbed.

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[1] Cf. Bull. U. S. Geol. Survey, No. 35, p. 38, 1886.

CHAPTER V.

THE HYDROELECTRIC EFFECT OF CHANGES OF MOLECULAR CONFIGURATION.

INTRODUCTORY.

39. The hydroelectric method is usually regarded as the most delicate criterion for testing changes of molecular constitution in metals. Unfortunately its indications are, in the present instance, distorted by polarization. Polarization, moreover, is apt to be much larger than the effect to be studied, so that the observer is obliged to resort to methods of measurement in which a fair degree of constancy of the error in question may be assured. From this it follows that unless the hydroelectric forces are as large as the interval "glass hard" to "soft," the effect of strains which can not be applied without removing the wire or metal from the hydroelectric bath is not observable. For in such a case the polarization varies with each immersion. Moreover, certain strains, like the drawn strain, show different mechanical conditions at different distances from the axis. Hence the hydroelectric constant of such a rod, were it obtainable, would be a complex magnitude.

In magnetization, the hydroelectric effect of which has been discovered by Remsen[1] and studied by Nichols[2], and more recently by Rowland and Bell[3], small hydroelectric effects ($<.03$ volts) can be detected because the metal during straining remains in place. Among other mechanical strains, traction, and perhaps torsion, admits of similar application to a metallic wire in place.

APPARATUS.

40. In the annexed figure 4 I have shown the apparatus used. *aac* and *bb* are consecutive pieces of a given kind of soft wire. Of these *aa* is to be stretched, *bb* examined in the homogeneous state. Hence *aa* is fixed between two points, of which the lower is on the circumference of an iron drum, *D*, which can be rotated by aid of the lever *LL* and frictionally fixed in position after any rotation. Usually the arcs of rotation of *D* were 180°, and four or five such strains could be applied to the wire consecutively before rupture ensued.

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[1] Remsen: Am. Chemical Journal, III, p. 157, 1881.
[2] Nichols: Am. Jour. Sci., XXXI, p. 272, 1886; ibid., XXXV, p. 290, 1887.
[3] Rowland and Bell: Phil. Mag. (5), XXVI, p. 105, 1888.

Before and after each of these strains measurements of hydroelectric state were made. For this purpose both wires are surrounded by glass tubes *AA* and *BB* respectively, held together by aid of the little block of wood *C*. These tubes were closed below with rubber corks through which the wires passed without leakage. The tubes were filled either with a concentrated solution of zinc sulphate, or with distilled water, or other material which does not act strongly on the metal. The electrolytic connection between *AA* and *BB* is made by a siphon, *S*, filled with the liquid of the tubes and closed at *s* with a parchment septum. The upper ends of the wires *b* and *c* were in connection with the terminals of a Mascart electrometer, or with the properly adjusted wires of an apparatus for a zero method.

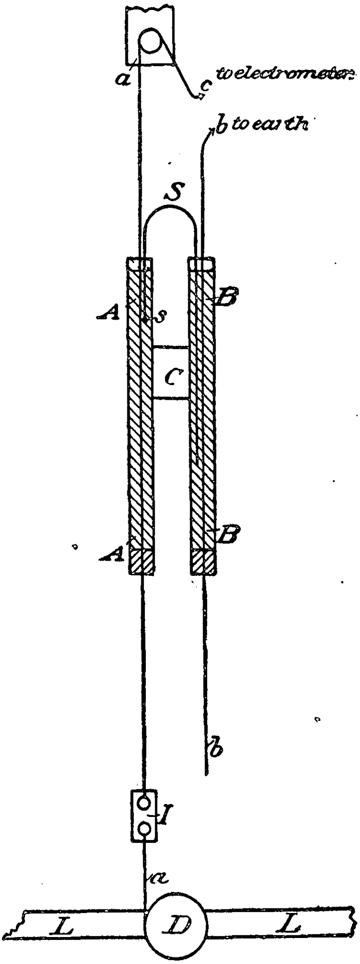

FIG. 4. Apparatus for measuring the hydroelective effect of stretching.

After straining the wire *aac* to the point of breakage, the apparatus was reversed and *bb* now strained in the same manner. In this way the number of distinct measurements for each adjustment could be doubled.

The wire being 54^{cm} long and the diameter of the drum about 1.7^{cm} the extension of wire per rotation of 180° was approximately 2.6^{cm}, or $\delta L/L=.05$ nearly. The amount differed slightly when wires of different thicknesses were used. The reduction of diameter of iron wire before and after straining to breakage is therefore considerable.

EXPERIMENTS.

41. *Zero method.*—In communicating my results I will omit the data obtained galvanically by the zero method. For the polarization disturbances are here of larger order than in electrometric work, an annoyance which vitiates the greater delicacy of measurement. The remark, however, is not superfluous that all the results were found to corroborate the electrometric data.

42. *Results for iron.*—The hydroelectric effect of traction is characterized by a temporary and a more or less permanent part. The temporary part may be given by observing the differences of potential at the end of each minute after straining, as well as the throw of the needle

immediately after. The difference of potential which remained when the temporary effect had subsided I called the permanent part. An allowance of five minutes was usually regarded sufficient. Of course this assumption is arbitrary; but whatever errors are committed are of like effect throughout the series. The value of the throw is expressed in volts, as are the other data. In all I made about 7 series of this kind, two of which are given in Table 20. The diameter of the iron wires before straining was $2\rho_s = {\cdot}086^{cm}$; after breaking $2\rho_h = {\cdot}078^{cm}$.

TABLE 20.—*Hydroelectric effect of tensile strain.*

IRON WIRE.

Strain.	$e\times10^3$ temporary.					$e\times10^3$ permanent.	Strain.	$e\times10^3$ temporary.					$e\times10^3$ permanent.
	Throw.	1^m	2^m	3^m	4^m			Throw.	1^m	2^m	3^m	4^m	
0	......	......	......	......	......	+ 9	0	......	......	......	......	......	+ 0
I	—34	......	......	......	......	+ 7	I	—18	......	......	......	......	+ 5
II	— 0	......	......	......	......	+11	II	— 2	......	......	......	......	+ 9
III	+ 8	......	......	......	......	+14	III	+ 5	......	......	......	......	+11
IV	......	......	......	......	......	+ 0	IV	+10	......	......	......	......	+13
0	......	......	......	......	......	—14	0	......	......	......	......	......	— 6
I	—26	......	......	......	......	—13	I	—15	......	......	......	......	— 1
II	— 0	......	......	......	......	— 8	II	— 0	......	......	......	......	— 0
III	+10	......	......	......	......	— 4	III	+ 2	......	......	......	......	+ 2
IV	+12	......	......	......	......	— 1	IV	+ 5	......	......	......	......	+ 3

Extension, $\delta L / L = {\cdot}05$ per pull.
Radial contraction, $\delta\rho / \rho < {\cdot}03$ per pull.
Mean permanent potential increase $= + {\cdot}003$ volts per pull.

The character of the data of table 20 is such as to indicate superimposed permanent and temporary effects. The former is distinctly electropositive in all my results; negative differences of potential are numerically decreased, positive differences increased. The increase of electropositive quality takes place simultaneously with the increase of length, at a rate which varies somewhat in the different experiments, but the mean value of which is about .003 volts per pull of the extension $\delta L/L = 0{\cdot}05$. This is equivalent to a decrease of the wetted external surface of the wire of about 5 per cent, provided there be no change of volume. The measured value is less than this, for the circumference before straining was found by aid of the micrometer to be $2\pi\rho_s = .27^{cm}$ and after straining $2\pi\rho_h = .24^{cm}$ as an aggregate of four pulls. This corresponds to less than 3 per cent of diminution of the wetted surface per pull.

The temporary effect is equally definite in character. Independently of the value of the permanent effect, the former is at first invariably negative, which quality is successively reduced, until finally the value, having passed through zero, becomes positive. The intensity of the first negative throw is strong; as a rule more so than the final positive throw.

DISCUSSION OF RESULTS.

43. Having thus obtained some knowledge of these phenomena for iron, it is expedient to indicate in passing some reasons for their probable cause. Iron submerged in any aqueous solution is polarized positively by a coat of hydrogen. Hence it is practically a condenser, whose capacity increases directly with the *wetted* surface, cæteris paribus. The effect of strain is therefore of a twofold kind: In consequence of the jarring and vibration which unavoidably accompany the stretching, some of the hydrogen is mechanically shaken off, and the positive potential or positive polarization decreased to a lower limit. Hence the *negative* throw after the first strain. Simultaneously with this result the capacity of the wire is diminished in consequence of stretching. Hence the positive potential or positive polarization is increased. If this last effect gradually predominates over the other (effect of jarring), the temporary throw changes from negative to positive.

This explanation is nearest at hand, and it need not be sufficient; but it is clear at once that before any hydroelectric effect can be ascribed to strain *as such*, it is necessary, to evaluate the polarization effect, as well as other minor errors, such for instance as are due to the increase of temperature of the wire during stretching. (Cf. Wiedemann's "Elektricität," vol. II, p. 773, etc.)

DATA FOR DIVERS METALS.

44. In the following tables I have inserted data corresponding to Table 20, but obtained with German silver, brass, copper, iron, all the wires being of larger diameter than before. The notation is the same as above. In Tables 21 to 24 zinc sulphate in concentrated solution is the electrolyte; in Tables 25 to 27 distilled water is used. At the ends of tables, the mean values per pull of extension ($\delta L/L$), radial contraction ($\delta\rho/\rho$), permanent potential increase *e* volts, are inserted for each wire.

TABLE 21.—*Hydroelectric effect of tensile strain.*

German silver, zinc sulphate, $\left\{ \begin{array}{l} 2\rho_s = \cdot 102^{cm}. \\ 2\rho_h = \cdot 093^{cm}. \end{array} \right.$

Strain.	$e \times 10^3$ temporary.					$e \times 10^3$ permanent.
	Throw.	1^m	2^m	3^m	4^m	
0	....	....	....	....	....	+27
I	+36	12	12	13	16	+28
II	+42	16	6	— 4	—19	+35
III	+50	19	—1	—10	—18	+47
IV	+69	42	18	9	2	+51
0	....	....	....	....	....	+24
I	+32	13	7	4	4	+30
II	....	....	....	....	....	+26
III	....	....	....	....	....	+24
IV	....	....	....	....	....	+23
V	....	....	....	....	....	+18

$\delta L/L$ = Extension per pull = .05.
Radial contraction per pull = .02.
Mean permanent potential increase per pull = .005.

TABLE 22.—*Hydroelectric effect of tensile strain.*

Brass, zinc sulphate, $\begin{cases} 2\rho_s = \cdot166^{cm}. \\ 2\rho_b = \cdot157^{cm}. \end{cases}$

Strain.	$e\times10^3$ temporary.					$e\times10^3$ permanent.
	Throw.	1^m	2^m	3^m	4^m	
0	......	......	......	......	......	+23
I	+21	18	12	12	13	+39
II	+41	31	28	25	24	+59
III	+48	30	20	18	15	+65
IV	......	......	......	......	......	......
0	......	......	......	......	......	—15
I	+17	4	2	0	—2	—18
II	18	10	6	3	1	—18

$\delta L/L$ = Extension per pull = ·05.
Radial contraction per pull = ·015.
Mean permanent potential increase per pull = ·015.

TABLE 23.—*Hydroelectric effect of tensile strain.*

Copper, zinc sulphate, $\begin{cases} 2\rho_s = \cdot166^{cm}. \\ 2\rho_h = \cdot150^{cm}. \end{cases}$

Strain.	$e\times10^3$ temporary.					$e\times10^3$ permanent.
	Throw.	1^m	2^m	3^m	4^m	
0	......	......	......	......	......	+4
I	0	0	0	0	0	+6
II	0	0	0	0	0	+6
III	+3	2	1	2	2	+6
IV	+2	2	......	......	......	......
0	......	......	......	......	......	—6
I } II }	+2	2	2	2	......	+0
III } IV }	2	2	2	......	......	—1

Extension per pull = ·05.
Radial contraction per pull = ·025.
Mean permanent potential increase per pull = ·001.

TABLE 24.—*Hydroelectric effect of tensile strain.*

Iron, zinc sulphate, $\begin{cases} 2\rho_s = \cdot156^{cm}. \\ 2\rho_h = \cdot147^{cm}. \end{cases}$

Strain.	$e\times10^3$ temporary.					$e\times10^3$ permanent.
	Throw.	1^m	2^m	3^m	4^m	
0	......	......	......	......	......	+8
I	—58	—42	—29	—22	—17	—6
II	—36	—24	—12	— 1	— 5	—5
III	—22	— 3	— 2	— 2	— 1	—3
IV	—36	—24	—17	—14	—10	—7
0	......	......	......	......	......	+4
I	—52	—38	—24	—18	—15	—7
II	—30	—17	—10	— 6	— 4	—7
III	—30	—18	— 6	— 4	— 0	—7
IV	......	......	......	......	......	......

Extension per pull = ·05.
Radial contraction per pull = ·015.
Mean permanent potential increase per pull = ·003.

TABLE 25.—*Hydroelectric effect of stretching.*

Brass, water $\left\{\begin{array}{l} 2\rho_s = \cdot 166^{\text{cm}}. \\ 2\rho_b = \cdot 154^{\text{cm}}. \end{array}\right.$

Strain.	$e \times 10^3$, temporary.					$e \times 10^3$, permanent.
	Throw.	1^m	2^m	3^m	4^m	
0	....	....	....	....	....	—76
I	+82	73	59	48	39	—44
II	+58	40	22	8	—2	—52
III	+63	49	28	14	7	—56
IV	+62	44	27	14	8	—60
0	....	....	....	....	....	+73
I	+42	42	42	38	36	+103
II	+21	14	13	8	6	+91
III	+28	21	11	—1	0	+77
IV	+29	24	14	7	3	+67

Extension per pull = ·05
Radial contraction per pull = ·02
Mean permanent potential increase per pull = ± ·015

TABLE 26.—*Hydroelectric effect of stretching.*

Iron, water $\left\{\begin{array}{l} 2\rho_s = \cdot 135^{\text{cm}}. \\ 2\rho_b = (.126^{\text{cm}}.) \end{array}\right.$

Strain.	$e \times 10^3$, temporary.					$e \times 10^3$, permanent.
	Throw.	1^m	2^m	3^m	4^m	
0	....	....	....	....	....	+16
I	—17	+46	60	67	70	+79
II	—10	+24	28	29	....	+95
III	....	....	....	....	....	....
IV	....	....	....	....	....	....
0	....	....	....	....	....	—56
I	—33	—17	— 6	—3	—1	—40
II	— 4	+ 7	+14	....	....	—23
III	— 6	+13	+14	....	....	— 6
IV	....	....	....	....	....	....

Extension per pull = ·05
Radial contraction per pull = ...
Mean permanent potential increase per pull = + ·027

TABLE 27.—*Miscellaneous work.*

Copper wire, water.

Strain.	$e \times 10^3$, temporary.					$e \times 10^3$, permanent.
	Throw.	1^m	2^m	3^m	4^m	
0	....	....	....	....	....	+15
Jerk	—42	+ 2	....	....	....	+ 4
Jerk	—35	— 4	....	....	....	+ 2
I, II	+29	+28	+29	+34	....	+27
III, IV	+13	+ 9	+ 7	+ 8	....	+28

Extension per pull = ·05
Radial contraction per pull = ·03
Potential increase per pull = ·015

TABLE 27.—*Miscellaneous work*—Continued.

Brass wire, water.

Strain.	$e\times10^3$, temporary.					$e\times10^3$, permanent.
	Throw.	1^m	2^m	3^m	4^m	
0						− 8
Jerk	—21					—25
Jerk	—35					—29
Jerk	—17					—21
Rub						—10
Rub						− 6
Rub						− 9
0						− 6
I	+35	35	35	31	31	+25

Iron wire, water.

0						—40
Jerk	—42	—15	− 6	+ 2		—39
Jerk	—49	—28	− 6	+ 1		—36
Jerk	—45	—21	− 7			—36
After waiting						—18

German silver, $2\rho = \cdot080^{cm}$. Zinc sulphate.

Strain.	$e\times10^3$, permanent.	Strain.	$e\times10^3$, permanent.
0	+13	0	—1
I	+ 7	I	—6
II	+ 0	II	—6
III	− 6	III	—6

EFFECTS CLASSIFIED.

45. Turning first to the permanent hydroelectric effect of traction, Tables 21 and 22 show increments of decidedly larger positive value than hold for iron in Table 20. The effect for copper in Table 23 is nearly zero, and for iron, Table 24, actually negative. Whatever the effect may be it is necessarily to be considered doubly specific, depending both on the metal and the liquid. Hence I made further investigations in Tables 25, 26, 27, by replacing zinc sulphate solution by distilled water. Here it is found that the permanent effect is decidedly less in magnitude for zinc sulphate than for water, from which a close relation of these phenomena and of polarization may be inferred. Moreover, the effect in case of water is by no means as regular as in the other case. In Table 25, for instance, the permanent points inclose an area of rhomboidal outline, showing that the effects of initial pulls are different in sign from those of final pulls. Again, copper, which in case of zinc sulphate is not charged by traction, shows a hydroelectric effect in case

of water comparable with that of other metals. Again the changes iron-water are excessively large. Irrespective of sign, the magnitude of the hydroelectric effect has increased with the diameter of the wires used.

Among results bearing on a later paragraph (§46) I may mention that the permanent effect of traction of iron in zinc-sulphate is sometimes positive and sometimes negative, depending on the qualities of the wire. Table 27 shows a specimen of German silver in which the permanent effect is negative.

I have given the temporary effects in their *absolute* values (increments) at consecutive times, independent of the potential of the wire. In case of German silver, of brass, of copper, these effects are distinctly positive, i. e., opposite in sign from the temporary effects for iron, which are invariably electro-negative both in the present instances (Tables 24, 26) and in Table 20.

DISCUSSION OF ERRORS.

46. Returning to the explanation suggested above (§ 43), it appears that in German silver, copper, and brass the effect of diminished capacity and of exposure of fresh surface,[1] due to stretching, both of which are positive, predominates over the negative effect of accidental jerking. In iron they do not so predominate. It is specially to be noticed that the permanent effect is entirely independent of the temporary effect. Inasmuch as the permanent effect is obtained by commutation (each electrode being alternately put to earth) the residuum of the temporary effect is discharged. From this it may be conjectured that the apparatus acts like a double condenser.

In Table 27 I give some data bearing on the probability of this explanation. The wires were adjusted in the usual way, but instead of being stretched they were only jerked by the action of the machine. In this case a negative temporary effect is obtained in all the metals, about of the same numerical order as the data of the earlier tables. Similar results follow after rubbing immersed parts of the wires.

Again, the temporary effect may be due to friction at the axle of the drum. But such an effect would discharge itself to earth, unless the wire and water act as a condenser. It would necessarily fall out of the permanent effect, for here the wires are alternately put to earth.

47. *Variable capacity.* If the wire be of the form of a cylinder of length l and radius r, its capacity is approximately

$$C = l \,/\, 2\, ln \frac{1}{r}.$$

Hence, since the charges are constant

$$Q = VC = V'C' \text{ or } V/V' = \log r / \log r'$$

whence it follows that (V_1' and V being identical)

$$V_1' = \frac{\log r'}{\log r - \log r'}(V - V') \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (1)$$

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[1] This being at once acted on by the liquid, falls under the considerations made in the text.

From this expression the polarization of the wire may be calculated from the difference of potential produced by traction. The data of Tables 20 to 27 then furnish the following values of V'. The subscripts attached to the symbols for metals refer to the number of the table.

TABLE 28.—*Digest.*

Metal.	Fe_1	Arg_2	Br_3	Cu_4	Fe_5	Br_6	Fe_7	Cu_8
log r/log r/r'	26	26	33	19	32	25	30	19
$\Delta V \times 10^3$	3×4	5×4	15×4	1×4	−3×4	±15×4	27×4	15×4
V_1'	+·31	+·52	+1·98	+·08	−·38	±1·50	+3·24	+1·14
	Zn SO_4					H_2O		

If the wire with its surrounding liquid acts like a condenser, of which the layer of polarizing gas (hydrogen) is the medium through which induction takes place, then the capacity is that of two concentric cylinders of radii r_2 and r_1, respectively, and the common length l. Here $C=\frac{1}{2}\frac{Kl}{ln\, r_2/r_1}$, or $C=\frac{r_1 l}{e}\left(1+\frac{e}{2r_1}\right)$, nearly, when $r_2-r_1=e$ and K, the specific inductive capacity of the layer of gas is taken as 1. Now, if we proceed as above, and consider the charge constant, an equation similar to (1) may be obtained by introducing some reasonable postulate relative to the thickness e of the polarizing gas. Suppose $e=$ constant; i. e., that before and after each pull the layer has not changed in thickness. Then $V/V'=(2r'+e)/(2r+e)$, or, approximately (V_2' and V' being identical),

$$V_2'=\frac{r}{r'-r}\,(V-V') \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Again, suppose the mass of gas to remain the same, so that $2\pi re=2\pi r'e'$. Then $V/V'=(2r'^2+er)/(2r^2+e)$, or, approximately (V_3' and V' identical),

$$V_3'=\frac{r^2}{r'^2-r^2}\,(V-V') \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Hence, Tables 1 to 8 furnish the following digest:

TABLE 29.—*Digest.*

Metal.	Fe_1	Arg_2	Br_3	Cu_4	Fe_5	Br_6	Fe_7	Cu_8
$r/(r'-r)$	39	42	71	38	67	51	57	38
V_2'	·12	·21	1·06	·04	−·20	±·76	1·54	·57
$r^2/(r'^2-r^2)$	75	77	136	72	127	100	110	72
V_3'	·22	·38	2·04	·07	—·38	±1·50	3·00	1·08
	Zn SO_4					H_2O		

In discriminating[1] between V_1, V_2, V_3, it is clear that the conditions

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[1] The close analogy of a polarized voltameter and a doubled condenser was pointed out by Varley (Phil. Trans., vol. CXLI, p. 129, 1872) and others. The subject is minutely discussed in Wiedemann's Elektricität, vol. II, pp. 758 to 771. It may be observed that in equation (2) the increment of potential varies as the decrement of the wetted surface.

under which V_1 applies are not given, and that the maximum probability rests with V_2; but this quantity is not decidedly above the order of possible polarization for the cases under consideration. Hence, the permanent hydroelectric effect due to a change of the electro-positive quality of a metal by traction, is obscured beyond recognition by the unavoidable variations of polarization accompanying the experiment.

SINGLE WIRES.

48. Having thus failed to obtain reliable evidence from the hydroelectric experiments, I endeavored with some pains to discern a direct electrical effect (potential) due to the traction of an insulated wire. Here again I failed; for not only is the needle of Mascart's electrometer always in motion when connected with a train of insulted wire, but the effect of traction is friction at the points of fastening at the ends of the wire. This friction of the metal wire against the insulators is apt to evoke relatively powerful charges as compared with the true effect of traction. Particularly is this the case if during traction the distended wire begins to loosen. By soldering loops at the ends of the wire the frictional disturbance can be reduced to a minimum, without, however, furnishing definite evidence of a purely traction effect.

SUMMARY.

49. In the above paragraphs I have endeavored to refer the very definite hydroelectric results obtained to the simplest explanation at hand. But it is necessary to bear in mind that the phenomena are so largely beyond the observer's control that an exhaustive experimental discussion is out of the question. It would be unwise, therefore, to lose sight of other points of view from which they may have a direct bearing on the real question in hand, viz., the possibility of molecular change in a metal corresponding to each change of strain imparted to it. The question is steadily gaining in probability. Osmond, after making an elaborate pyrometric study of the conditions under which Gore's phenomenon occurs in iron, postulates the existence of an α and a β variety of iron. These varieties when cold may be distinguished physically by their difference in hardness. Moreover, β-iron, besides being produced spontaneously out of α-iron, above a certain temperature in red heat, may also be produced in small quantity by straining α-iron at ordinary temperatures. I pointed out that such a hypothesis involves the occurrence of α and β varieties of most metals, even when no such criterion as is given by Gore's phenomenon is observable. Quite recently Mr. Carus-Wilson,[1] from experiments made on the viscosity of strained steel, summarizes his experience in favor of Osmond's[2] view. Unfortunately, the well known effects of strain on the thermo-

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[1] Carus-Wilson, Nature, vol. 41, 1890, p. 213.

[2] Osmond, Annales des Mines, July-August, 1888; Mém. de l'artillerie de la Marine, Paris, 1888, p. 4.

electric quality and on the resistance of metals are not at once interpretable, except, perhaps, in so far as they are accompanied by hysteresis (Cohn, Warburg, Ewing, Schumann). The ion theories of metallic electrical conduction now coming into vogue (J. J. Thomson, Giese[3]), conditioned as they must be by the occurrence of marked molecular instability in metals, are steps in the same direction. I will therefore merely point out, in concluding, that the simple explanations given above for the temporary effect, which was found consistently negative at first in iron, and consistently positive in all the other metals, is not satisfactory. It is permissible to regard it as the direct result of a change of molecule due to straining; for it is precisely in the first stages of the temporary effect that evidence for such molecular change may reasonably be sought.[4]

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[1] Giese, Wied. Ann. vol. 37, 1889, p. 576.

[2] Cf. Rowland and Bell (loc. cit.), who are obliged to base their inferences on the temporary hydroelectric effect of magnetization. In all problems of this character it is necessary to distinguish between the positional stability and the chemical stability of a molecule. It does not follow that if the former quality is increased the latter will also be, for a chemical solvent does not pick up molecules bodily, but by disintegrating them. In certain experiments on the isothermal electromotive force of a Daniell between 10 and 1,800 atmospheres, I will indicate this further.

CHAPTER VI.

THE SECULAR ANNEALING OF COLD HARD STEEL.

INTRODUCTORY.

Inasmuch as the method I used for testing Maxwell's theory of the viscosity of solids contains a proof of that theory a fortiori, I did not distinguish in that paper[1] between a break-up of configurations of molecular wholes and the more intensified break-up in which the integrity of the molecule itself is invaded. The experimental distinction is not always easy. If, for instance, I dissolve certain solids (pitch, say, in turpentine) I may produce a continuous series of viscous fluids; but the molecular mechanism by which this is brought about can not in the present state of our knowledge of solution be said to be known. I may cite another striking example, ebonite, which above 100° loses vicosity at an exceedingly rapid rate by mere heating; but, again, the molecular change which produces the viscous effect is obscure. And so generally in less remarkable experiments.[2] In the case of metals, it appears that those elements whose molecules are least stable and possibly monatomic[3] (K, Na, etc.) are of a soapy consistency, so that here vicosity (Nachwirkung) and permanent set can hardly be distinguished. In general it appears that metallic permanent set is physical manifestation of looseness of molecular structure. If, as in the case of annealing glass-hard steel, the rigid arch (say) of molecular wholes breaks up because one or more of the molecules, the stones of that arch, disintegrate, and if the decomposition be of a kind that the débris may be chemically recognized, then, by coordinating the viscous and the chemical observations, I obtain a fairly good notion of the molecular mechanism which has produced the viscous effect. This is the method I applied to prove Maxwell's theory. But partial disintegration or reconstruction of molecules may easily be conceived to occur in such a way as to escape detection altogether or at least to escape detection as much as does a break-up of configurations of molecular wholes. It may, I think, be reasonably supposed that the solid molecule is of the form M_n, in which n is variable; and any given value of n will occur

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[1] Philosophical Magazine, London, August, 1888.

[2] Cf. Lothar Meyer (Die modernen Theorien der Chemie, Breslau, 1884, chapter VIII,) on solid molecular structure.

[3] Ibid. chapter XVI, sec. 308, etc.

less frequently according as it is proportionately greater or less than the mean or typical value of n for the solid. The effect of strain, of change of strain, or even of long continued secular subsidence is merely to vary the distribution of molecules M_n, so that the general properties of any observably finite part of the solid do not change.[1]

I will adduce other points of view in succeeding papers; but the suggestions stated are sufficient, I think, to show the importance of discerning whether the cause of viscous deformation in tempered steel is the type of viscous deformation in general or whether, in using the phenomena of annealing steel to test Maxwell's theory, I have merely interpreted the exception to prove the rule. The result of such an investigation, besides throwing light on the structure of solid matter, must ultimately lead to inferences bearing directly on the questions of fusion, solution, and volatilization.

RESULTS FOR HOMOGENEITY OF RODS.

51. This inquiry, being essentially a comparison of detail, will consume much time before it can be brought to an issue; and, as the individual parts of my work have led to results which are of interest[2] apart from the purposes to which I hope ultimately to apply them, it is perhaps best to communicate the data separately. The following results on the secular annealing of cold glass-hard steel essentially sustain the inferences of my last paper. They were omitted because of the space occupied by the discussions there given. The rods to which the data refer are of Stubbs's best steel, tempered in a special apparatus,[1] by aid of which the wire heated to redness electrically is suddenly whipped into water. Freshly quenched samples of wire showed specific resistances (0° C.) as high as $s=48$. All the rods were tested for longitudinal uniformity of temper by stepping off, as it were, the resistance of lengths of 2^{cm}. each for each of the consecutive 3^{cm}. of wire. The total length being about 25^{cm}., eight measurements were thus made. A device utilizing Matthiessen and Hockin's method, and provided with a suitable rider, enabled me to do this with reasonable accuracy. Table 30 contains the results as obtained with three batches of wire, of the diameters

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[1] In other words, it is here supposed that the assumption of solid state has not thoroughly eliminated the liquid or even the gaseous molecule and that it has, on the other hand, produced molecules of an ultra-solid complexity. Here I touch the keynote of certain difficulties in my mind against conceiving the solid molecule as a uniformly distinct whole, capable of rotation (Kohlrausch viscosity) or capable of translation from strained to isotropic configuration (Maxwell viscosity). I look upon it as a more cumbersome thing, which may under favorable conditions even lose its identity, and which, when undergoing the motions stated, comes into serious conflict with contiguous molecules. Such a view, even if it be mere surmise (excepting the case of hard steel discussed), is a suggestive working hypothesis; for it seems broad enough to enable me to circumscribe the true phenomenon by clipping the postulate. This is the general endeavor of my present work.

[2] It is well known that experiments on the secular changes of metals are being made at Glasgow by Mr. Bottomley. Cf. Brit. Assoc. Report, 1888, p. 537.

[3] Bull. U. S. Geol. Survey, No. 14, 1885, p. 29. My present apparatus is horizontal in form and enables me to quench the wires from any degree of red heat in water or other liquid at any desirable temperature. See Fig. 5, p. 7, Bull. No. 73, 1891.

$2\rho = {\cdot}081^{cm.}$, ${\cdot}044^{cm.}$, and ${\cdot}127^{cm.}$, respectively. The approximate resistance (microhms) of the $2^{cm.}$ of length is designated by r.

TABLE 30.—*Longitudinal uniformity of temper of the steel rods.—Variation from mean, in terms of the electrical interval, hard-soft.*

No. 1. r=18500.	No. 2. 18500.	No. 3. 17700.	No. 4. 17600.	No. 5. 17700.	No. 6. 18500.	No. 7. 18400.	No. 8. 18500.	No. 9. 17400.	No. 10. 17900.
·002	·002	·000	·003	·010	·005	·004	·009	·032	·006
4	— 2	0	— 2	10	— 3	1	— 11	18	— 6
2	— 2	5	— 2	— 7	— 7	1	— 11	11	2
— 1	2	5	7	— 2	5	7	5	— 46	2
— 6	— 2	5	— 2	6	1	7	— 3	— 64	— 2
4	— 6	— 13	— 6	— 7	— 2	— 5	5	— 16	— 6
1	— 2	0	— 2	— 11	— 7	— 8	5	23	10
— 4	10	— 4	3	2	9	— 5	1	41	— 6
No. 11. r=61200.	No. 12. 60600.	No. 13. 61200.	No. 14. 69200.	No. 15. 62000.	No. 16. 6800.	No. 17. 6760.	No. 18. 6580.	No. 19. 7290.	No. 20. 6850.
·007	— ·007	— ·003	·023	·016	— ·006	·001	— ·009	·001	— ·013
— 2	— 1	— 3	— 1	— 1	— 2	1	7	1	— 26
— 7	— 4	— 3	1	— 3	3	5	15	10	4
— 10	— 7	— 10	— 7	— 9	— 2	— 3	8	10	17
1	4	5	— 4	2	— 2	— 3	— 1	11	13
1	— 1	— 3	— 4	— 12	— 2	1	11	— 11	13
1	4	8	— 4	— 1	3	— 3	— 5	— 11	— 13
10	13	8	— 4	8	7	1	— 20	— 11	4

With the exception of No. 9, the variations are, as a rule, well within 1 per cent. of the electrical value of the interval hard-soft. Where the resistance is larger or smaller than the mean value, it is possible that the parts were accidentally splashed by the water immediately before quenching or quenched at a different degree of red heat. But, inasmuch as the series of measurements for each rod takes some time and as the effective resistances are necessarily small, I believe that the rods are even more homogeneous than Table I indicates; for the errors introduced by variations of temperature, by the difficulty of clamping the thin, very brittle rods (soldering would change the temper enormously), and by other inconveniences of manipulation, are by no means negligible. Hence the degree of homogeneity found may be considered quite satisfactory.

MASS CONSTANTS OF RODS.

52. In Table 31 I give the mass m, length l, and density at 0° C., Δ_0, of some of the rods. The latter datum is essential for the determination of the sections. I shall also use it in the future in determining the secular volume-changes of these wires. Rods Nos. 11 to 15 are too thin for direct measurement. Hence a mean value of Δ_0 was here assumed. I may add that in the soft state the density of these rods is about $\Delta_0 = 7{\cdot}80$.

TABLE 31.—*Mass constants of the glass-hard steel rods, June, 1885.*

No.	m	l	Δ_0	No.	m	l	Δ_0
	g.	*centim.*	*g/cm³.*		*g.*	*centim.*	*g/cm³.*
1	·9910	24·95	7·710	11	·3257	27·94	
2	·9544	24·02	7·689	12	·3322	28·30	
3	·9970	25·25	7·703	13	·3170	27·20	
4	1·0483	26·30	7·705	14	·2888	24·35	
5	1·0079	25·46	7·703	15	·3004	26·07	
6	1·0243	25·80	7·687	16	2·4713	25·63	7·676
7	1·0089	25·47	7·670	17	2·4857	25·70	7·671
8	1·0074	25·50	7·682	18	2·1043	22·50	7·544
9	1·0666	26·68	7·726	19	2·5327	26·06	7·685
10	1·0293	25·58	7·719	20	2·3557	24·40	7·653

53. *Electrical constants of rods.*—Table 32 contains the electrical constants of these rods; r_t being the observed resistance per centimeter at $t°$, α the temperature coefficient, and s_0 the corresponding specific resistance at 0° C. The wires were quenched on June 1 and 2, 1885, and the measurements made at the time given, only a few days after hardening. Sections and radius are given under q and ρ respectively. In most cases q is individually determined.

TABLE 32.—*Specific resistance of the glass-hard steel rods, measured June 4 and 8, 1885.*

[Effective length, 20 cm. to 26 cm.]

No.	$q\times10^6$	$2\rho\times10^3$	r_t	t	$\alpha\times10^3$	s_0
	Centim.²	*Centim.*	*Microhm.*	° *C.*		*Microhm.*
1	5152	80·6	9260	27·5	1·5	46·0
2	5168		9250	27·8	1·5	46·0
3	5126		8870	28·3	1·6	43·7
4	5173		8810	27·0	1·6	43·8
5	5139		8840	27·2	1·6	43·7
6	5165		9260	26·8	1·5	46·1
7	5164		9200	27·0	1·5	45·8
8	5143		9260	26·3	1·5	46·0
9	5174		8720	26·3	1·5	43·6
10	5214		8950	25·1	1·5	45·1
11	1520	44	30670	25·2	1·5	45·1
12	1520		30320	25·3	1·6	44·4
13	1520		30620	24·8	1·5	45·0
14	1520		30080	25·5	1·6	44·1
15	1520		30990	26·8	1·5	45·4
16	12560	126·5	3400	26·4	1·7	41·0
17	12610		3382	26·4	1·7	41·0
18	12400		4144	26·6	1·5	49·5
19	12650		3643	26·7	1·6	44·3
20	12620		3427	27·2	1·7	41·5

Finally, Table 33 contains the electrical constants of these rods made about thirty-seven months after the first measurement. It also contains the variations, Δr_t, of the resistance per centimeter, as well as the variations, Δs_0, of the specific resistance. It will be seen that Δs_0 is negative throughout, whereas the effect of atmospheric influence and the unavoidable abrasion in cleaning the surfaces of the wires before measurement would produce a positive error. The same bridge and the same standards of German silver are used both in the measurements of Table 32 and of Table 33. The fact that the wires differ in diameter, and therefore vary largely in resistance, is a guarantee against the effect of differences of sectional errors of the bridge wire. Again, although Δs_0 is essentially the difference of secular change between the steel-wire and the German-silver standards, the fact that two standards (1·0 ohm and 0·1, respectively) were used at least partially eliminates the error due to variations in the standards. Moreover, the electrical effects of corresponding variations of temper (steel) and of the drawn strain which the German silver may possibly carry are enormously different. For instance, if glass-hard steel is boiled long enough the change of resistance may reach 12 per cent and more. The effect of boiling German silver is of the order of some tenths per cent.[1] Hence I apprehend no serious error in ascribing the whole of the observed variation of s_0 in Table 33 to secular annealing of the glass-hard steel rods under experiment.

TABLE 33.—*Specific resistance of the glass-hard steel rods measured July 9, 1888, and the secular variation.*

[q as in Table 32; effective length, about 23 cm.]

No.	$2\rho\times10^6$	r_t	t	Δr_t	$a\times10^3$	s	Δs_0
	Centim.	*Microhm.*	° *C.*	*Microhm.*		*Microhm.*	*Microhm.*
1	80·6	8460	28	—790	1·7	41·7	— 4·2
2		8430		—820		41·7	— 4·3
3		8010		—860		39·3	— 4·4
4		7950		—850		39·3	— 4·4
5		8010		—830		39·4	— 4·3
6		8460		—800		42·0	— 4·1
7		8400		—800		41·5	— 4·3
8		8510		—750		41·9	— 4·1
9		7920		—800		39·2	— 4·3
10		8170		—780		40·8	— 4·3
11	44	27860	29	—2810	1·7	40·5	— 4·6
12		27710		—2610		40·3	— 4·2
13		28000		—2620		40·7	— 4·3
14		27490		—2590		40·0	— 4·1
15		28400		—2590		41·3	— 4·1
16	126·5	2807	29	— 590	2·1	33·3	— 7·7
17		2807		— 570		33·4	— 7·5
19		2830		— 810		33·8	—10·5
20		2808		— 620		33·5	— 8·0

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[1] Cf. Bulletin U. S. Geol. Surv. No. 14, p. 94.

SUMMARY.

54. Summarizing the results of Tables 32 and 33, it appears that during the 37 months between the two series of observations the specific resistance of the rods has fallen from 46·5 to 42·5 in case of the thin rods (diameter $<$·08 centim.) and from 43·7 to 35·4 in the case case of the thicker rods (diameter .13^{cm}.). Hence the variations are a decrement of specific resistance amounting to some 10 or even 20 per cent in the extreme cases. This may be stated succinctly as follows: Mean atmospheric temperature acting on freshly quenched steel for a period of years produces a diminution of hardness about equal to that of 100° C. acting for a period of hours. Similar results have been suspected for magnetic measurements; but such results are very much less easily interpretable than the electrical data of Table 33; for earlier measurements prove conclusively that the electrical variations in question are sufficient evidence for the occurrence of concomitant changes of hardness; volume, carburation, etc. Finally, the above results show that the method of tempering magnets proposed by Dr. Strouhal and myself warrants the steel against secular structural instability for a time certainly exceeding three years.

CHAPTER VII.

THE VISCOSITY OF ELECTROLYZING GLASS.

APPARATUS.

55. The apparatus by which I endeavored to throw light on this question is represented in Figs. 5 and 6. As regards principles involved they are identical with my earlier apparatus. Hot and cold parts of a glass tube *abc* are counter twisted. To accomplish this with least amount of breakage, the ends of the tube are clamped between parallel thin boards, *A* and *B*, and cemented with mastic. *A* being fixed, torsion is applied at *B*. The amount of this is never very large and it may be gradually increased by a screw adjustment acting against a radial lever in connection with *B*. The experiment is troublesome, as the brittle glass tubes frequently break. To heat any part of *abc*, it is inclosed in one of my boiling tubes, *dddd*, containing mercury, *GG*, which may be kept in ebullition by the ring burner *RR*. The mirror *M*, adjustably fixed between hot and cold parts of *abc*, registers the amount of viscous deformation. The method of passing current through the tubes is different in the two figures. The more complicated arrangement in Fig. 5 secures greater constancy of temperature along cold parts of the tube, all hot parts being above. The core of the tube *abc* is partly filled with sodium amalgam, as shown at *ff''f'*, and one terminal of a dynamo, or a Grove battery, connects with this at *f'*. Again the tube *abc* is surrounded near its middle by a funnel-shaped cup *FF*, also containing sodium amalgam. This can be drawn up into the central tube *gg*, closed above by aid of an exhaust pipe attached at *E*. The other terminal of the dynamo is in connection with *F*, as shown at *h*. When this current is made, it therefore passes in at *f'*, into the core of *abc*, *through abc*, into the core of *gg*, into the cup *F*, and thence back to the dynamo. In Fig. 6 the mechanism is much simpler. The tube *abc* is fixed in *dddd* with a plug of plaster of paris, *p*, and *abc* is immediately surrounded by the ebullition mercury *G*. The current as before passes in at *f'*, through the walls of *abc* into *G*, and thence via *h* to the dynamo. Some care must here be taken in screening *M*, the mirror. In general a number of screens are to be disposed in ways which easily suggest themselves.

RESULTS.

56. In Table 34 I have given my first results with the apparatus, Fig. 5. A battery of 10 Grove cells was used as a source of current. Warburg's[1] device of sodium amalgam electrodes was not known to me at the time, and I here used simple mercury for the purpose. The current in this case was originally about ·01 ampère, but fell off rapidly to ·001 ampère, and finally vanished altogether. The results of the table were obtained during the period of current; and although in later experiments I applied both dynamo and intermittent currents, the effects were nil. Warburg (loc. cit.) has shown that glass partially electrolyzed is a condenser of very measurable capacity, the dielectric being filmy silica. In the table, L is the length of the tube, a the length of the hot part (temperature $\theta = 360^\circ$), and k the length of the cold part (temperature $\theta' = 25^\circ$), respectively. The mirror is at a distance l' above the lower end. The rate of twist is τ. Finally ρ_1 is the outer radius, ρ_2 the inner radius, q the material section of the tube. To understand the progress of the experiment it is necessary to consult the time column. The viscous datum has the same meaning as above, except that in the present instance it refers to relatively very large sections q. Hence the smaller amounts of viscous motion observed. Moreover, in case of glass, τ can only be chosen very small, if liability to rupture is to be avoided.

In Table 35 the dimensions of apparatus are nearly the same as in Table 34. Twist, however, was considerably increased, almost sufficiently to produce rupture; and, moreover, sodium amalgam is here employed. The result was a current of the uniform intensity of 0·02 ampère traversing the glass.

A number of other similar experiments were made, all of which led to

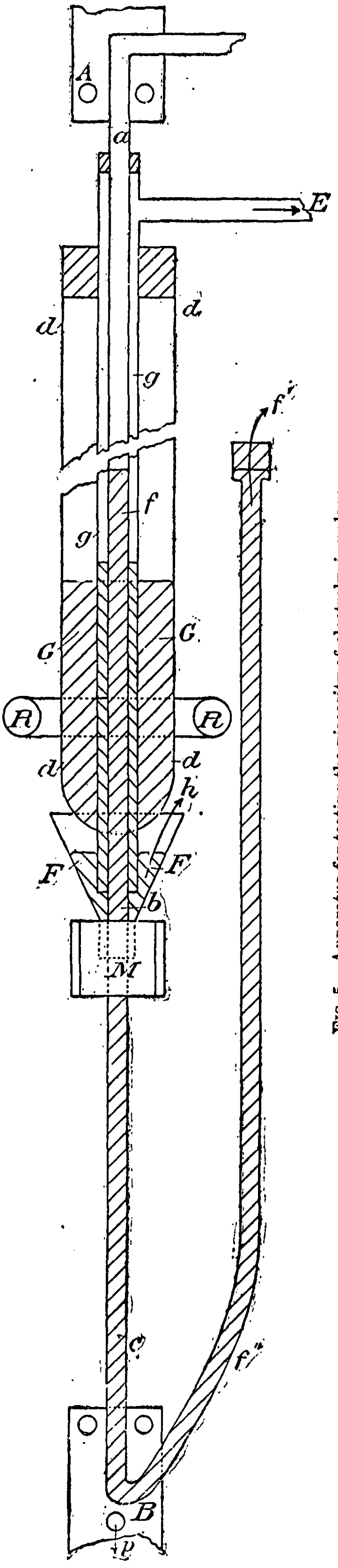

FIG. 5.—Apparatus for testing the viscosity of electrolyzing glass.

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[1] Warburg: Wied. Ann., xxi, p. 622, 1884.

results of the same indecisive character. With currents of the small intensity given (<0·02 ampère), viscous effects can hardly be expected to be discernible within the small interval of observation. If large intervals were chosen constancy of temperature in case of the apparatus given could not be guaranteed. The results of Table 34 are such as to suggest the actual occurrence of a viscous effect of current. This is not substantiated by Table 35. I can not, however, regard these results as conclusively negative. It is difficult to avoid contact between the tubes *abc* and *gg* in Figure 5, without choosing for the latter a tube inconveniently wide. For this reason I abandoned this apparatus and made the further experimentation with that of Fig. 6. It will not be necessary to give the data in full. They are again indecisive, because the viscous motion is too slight for sharp discrimination. The method of work being such that the rate of twist was successively increased until rupture finally ensued, it appears that the experiment was carried quite up to the limits of attainable accuracy. In Table 36 I indicate the nature of the results for the case of an extreme intensity of twist, after which the tube broke.

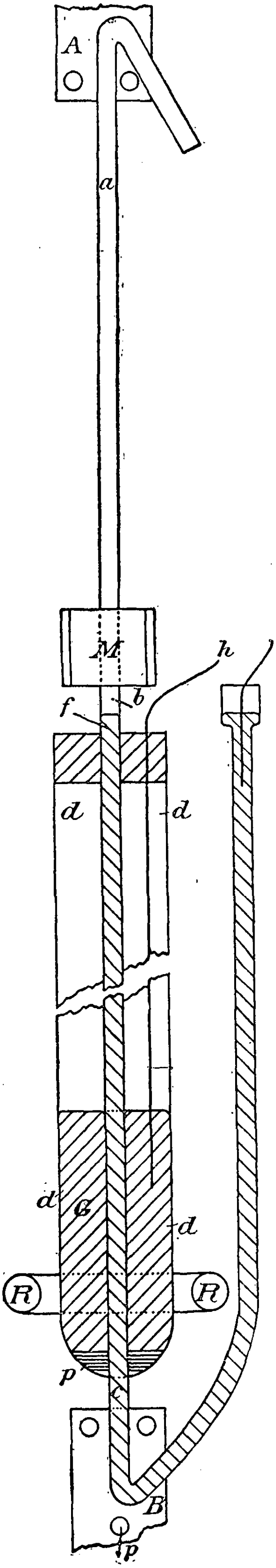

Fig. 6.—Apparatus for testing the viscosity of electrolyzing glass.

INFERENCES.

57. To summarize: When the available current can not be increased beyond the small datum given in the tables, it is improbable that viscous effect of larger value than one or more per cent is possible; but, to discern such small differences, the viscous motion must be very much more rapid. In other words, very *thin-walled* tubes of small caliber are to be chosen. In such a case the intensity of current as well as the viscous deformation will be effectively increased. The difficulties of experiment with thin tubes are very great, so that I am obliged to abandon further research at present.

In conclusion I may insert some remarks relative to the conditions under which increased viscous motion during the passage of current may be expected. Prof. J. J.

Thomson and Mr. Newell[1] have shown that for small electromotive forces the leakage in case of a liquid dielectric obeys Ohm's law, thus indicating that the molecular break-up was merely directed, but not produced, by electromotive force. On the other hand Quincke, using much larger electromotive forces, finds that the leakage, cæteris paribus, takes place according to some higher power than the first of electromotive force. Hence in this case the electric field is actually instrumental in dissociating molecules.[2] Since Ohm's law is rigorously obeyed in electrolytes, it is questionable whether electromotive forces of ordinary value can produce viscous effects even in case of solid electrolytes, for the rate of break-up is not thereby increased.

TABLE 34.—*Viscosity of electrolyzing glass. Hg terminals.*

$L=95^{cm}$; $a=15^{cm}$; $k=45^{cm}$; $l'=40^{cm}$; $\theta=360°$; $\theta'=25°$; $\tau=0{\cdot}003$; $\begin{cases} 2\,\rho_1=0{\cdot}40^{cm} \\ 2\,\rho_2=0{\cdot}30^{cm} \end{cases}$

Time.	Current.	$\frac{\phi-\phi'}{\tau}\times10^3$	Time.	Current.	$\frac{\phi-\phi'}{\tau}\times10^3$
12h 10m	off	0·0	12h 35m	on	82·3
17		18·0	38		87·3
20		29·7	38	off	87·3
23		43·0	41		90·7
23	on	43·0	41	on	90·3
26		56·3	44		92·3
26	off	57·0	44	off	93·0
29		67·0	47		94·3
29	on	68·3	47	on	94·3
32		78·3	50		96·3
32	off	77·7			
35		82·3			

Now, unless the electric field be of sufficient intensity to produce a marked change in the motion, i. e., the free path of the ion, it is not probable that such a field will modify the viscosity of glass. Fields of small intensity can not increase the molecular instability. Hence the experiments of the next chapter, the character of which is nearly the converse of the present experiments, are better calculated to show positive results.

TABLE 35.—*Viscosity of electrolyzing glass. Na-amalgam terminals.*

Time.	Current.	$\frac{\phi-\phi'}{\tau}\times10^3$	Time.	Current.	$\frac{\phi-\phi'}{\tau}\times10^3$
3h 20m	off	0·0	3h 51m	on	9·2
32		5·2	52		9·4
41		6·8	52	off	9·4
45		8·4	53		9·6
47		8·8	53	on	9·6
49		8·4	54		9·6
49	on	8·4	54	off	9·6
50		9·0	55		9·6
50	off	9·0			
51		9·2			

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[1] Thomson & Newell: Proc. Roy. Soc., XLII, p. 410.

[2] Cf. J. J. Thomson: Application of dynamics to physics and chemistry, p. 292.

TABLE 36.—*Viscosity of electrolyzing glass. Na-amalgam terminals.*

$\theta = 360°$. $2\rho_1 = \cdot 53^{cm}$. $a = 15^{cm}$.
$\theta' = 25°$. $2\rho_2 = \cdot 40^{cm}$. $L = 95^{cm}$.
Current, 0.02 ampère.

Time.	Current.	$\frac{\phi-\phi'}{\tau} \times 10^3$	Time.	Current.	$\frac{\phi-\phi'}{\tau} \times 10^3$
34^m ... 36....	off....	1·0	46.... 48....	off....	3·8
36.... 38....	on	1·6	48.... 50....	on	4·8
38.... 40....	off....	1·8	50.... 52....	off....	5·2
40.... 42....	on	2·4	52.... 54....	on	6·0
42.... 44....	off....	2·6	54.... 56....	off....	6·8
44.... 46....	on	3·2	56.... 58....	on	7.6

CHAPTER VIII.

THE ELECTRICAL RESISTANCE OF STRESSED GLASS.

INTRODUCTORY.

58. The thermal relations of the resistance of glass, originally studied by Buff,[1] have more recently been made the subject of research in memoirs by Beetz,[2] Foussereau,[3] Perry,[4] Thomas Gray,[5] and others. Warburg's[6] experiments, however, throw new light on the inquiry, by showing that the apparent polarization evoked by the passage of current is due to a layer of nonconducting silica depositing at the anode. If this be continually dissolved by an electrode of sodium amalgam, the apparent polarization is so far removed that an almost constant current may be kept up indefinitely. If the film be not removed, conduction soon ceases and the glass behaves like a condenser of measurable capacity.

The effect of temperature on the conductivity of glass has thus been mapped out with considerable detail, and it will be superfluous to add new data in the following chapter. I purpose therefore to confine myself narrowly to the effects of stress[7] on electrolyzing glass, kept as nearly as practicable at different constant temperatures between 100° and 360°.

APPARATUS.

59. The apparatus for these measurements are shown in Figs. 7, 8, 9, 10, 11. Figs. 7 and 8 are simpler and adapted to 360° and 100° respectively. Figs. 9 and 10 are intended for experiments with aniline (186°) or other nonconducting fluid, boiling at higher temperatures; and the last apparatus, Figs. 10, 11, are differential in kind.

As before, the ends of the tube *abc* (Fig. 7) to be operated upon are bent hook-shaped, and then fastened by screws and resinous cement between

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[1] Buff: Lieb. Ann., vol. xc, 1854, p. 257.

[2] Beetz: Pogg. Ann., Jubelband, 1874, p. 23.

[3] Foussereau: Jour. de phys., II, vol. xi, 1883, p. 254.

[4] Perry: Proc. Roy. Soc., vol. xxiii, 1875, p. 468.

[5] T. Gray: Proc. Roy. Soc., vol. xxxiv, 1883, p. 199.

[6] Warburg: Wied. Ann., vol. xxi, 1884, p. 622; ib., xxxv, 1888, p. 455.

[7] Reference may here be made to J. and P. Curie (C. R., vol. 91, pp. 294, 383; vol. 92, p. 350, 1881; vol. 93, p. 1137, 1881), and to Hankel (Wied. Ann., p. 640, 1881), who show that in certain hemihedral crystals longitudinal compression is accompanied by the manifestation of electromotive force. Curie's very recent work is summarized in the Beiblätter, vol. 12, p. 857 to 867, 1888.

slabs of wood *A* and *B*. The upper one is fixed; the lower, *B*, provided with a hook from which a scale pan may be hung. In the experiments made, the load *P* was gradually increased as far as 20 kg. To heat the tube *abc*, and thus promote conduction, I used a ring burner *RR*, as before. *GG*, the ebullition liquid (here mercury), is contained in the boiling tube *d*, to the bottom of which the experimental tube *abc* is cemented with plaster of paris. Glass is electrically so sensitive to changes of temperature near 300°, that great care must be taken to keep the flame of the burner constant, and the ring is to be fixed in position relatively to the tube. Any disturbance of this symmetry during loading produces a periodic thermal error, the effect of which may be excessively large as compared with the stress effect to be measured. Finally, the current when made passes into the mercury within the tube *abc* at *f'*, then through the walls of the tube into the ebullition liquid *G*, and thence, via *h*, back to the battery. At 360° the resistance of this arrangement was less than 200 ohms, so that aside from temperature fluctuations the measurement is easy. With a single Daniell and a mirror galvanometer, the current observed is sufficiently constant to admit of direct measurement. From this the resistance may be deduced. When the liquid boils violently, resistance is variable, probably from the fact that a film[1] of mercury vapor of variable thickness envelops the metal and interferes with the uniformity of contact. The resistance for this case is larger, even twice as large, as when the mercury is at incipient ebullition. When the apparatus is loaded and unloaded alternately, relatively long and regular fluctuations of temperature are of no disturbing effect, the stress effect being superposed on the long undulation.

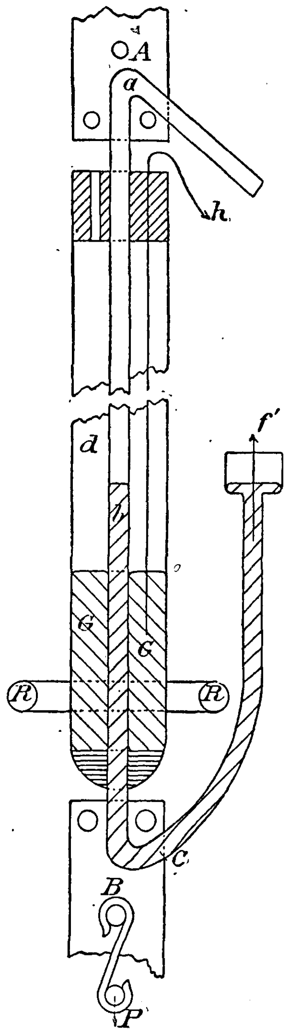

FIG. 7.—Apparatus for testing the viscosity of stressed glass.

EXPERIMENTS.

60. *Data for 350°.*—The scale deflections under the stated conditions are given below. From the many data I will select those of later date, these results being less liable to inaccuracy than the earlier data.

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[1] I have thought of using this observation as a boiling-point criterion.

TABLE 37.—*Resistance of glass across the lines of stress.*

[$\theta = 350°$. $2\rho_1 = \cdot 53^{cm}$. $2\rho_2 = \cdot 40^{cm}$. Resistance, 500 ohms.]

Time.	Load.	Deflection.	Time.	Load.	Deflection.
h. m.	*kg.*	*cm.*	*m.*	*kg.*	*cm.*
2 8	0	5·70	29	0	5·10
10	0	5·40	31	0	4·90
12	0	5·20	32	5	4·60
12	5	5·10	34	5	4·60
13	5	5·10	36	5	4·65
15	5	5·10	38	0	5·10
16	0	4·85	40	0	5·60
18	0	4·55	42	0	5·90
20	0	4·28	43	5	5·80
22	5	4·40	46	5	5·30
26	5	5·40	47	7	5·25
27	0	5·35	51	7	5·00

Plainly the chief fluctuations here observed are due to temperature; but whatever the stress effect may be, its amount can not exceed a few per cent of the resistance of the glass sample. This appears quite as clearly in other results of the same kind, which need not be summarized here.

61. *Data for 100°.*—In consequence of the thermal discrepancies enumerated, I made the next experiments at 100° in a steam bath. The resistance encountered under these circumstances is, of course, very large. I measured it at about 20,000,000 ohms in case of the apparatus, Fig. 8. Here the tube to be stretched, *abc*, is surrounded by a wider tube, *gg*, closed above and below. Both tubes contain sodium amalgam, protected from moisture[1] by a layer of paraffin, *m*. Steam enters at the top and is discharged at *S*, so that the apparatus is drained of condensed water. In other respects the present apparatus resembles the above. The scale pan is attached at *P*. The results for this case are much more uniform. I give the following example:

TABLE 38.—*Resistance of stressed glass at 100°.*

[$2\rho_1 = \cdot 53^{cm}$. $2\rho_2 = \cdot 40^{cm}$. $l = 15^{cm}$. Resistance, 20 megohms, approximately.]

Time.	Load.	Deflection.	Mean.	Time.	Load.	Deflection.	Mean.
h. m.	*kg.*	*cm.*	*cm.*	*m.*	*kg.*	*cm.*	*cm.*
10 50	0	5·50		12	20	5·35	5·36
53	0	5·45		14	20	5·35	
55	0	5·25		17	20	5·40	
60	0	5·33	5·30	20	20	5.33	
11 07	0	5·30		21	21	5·38	
10	0	5·28		23	21	5·37	
				Tube breaks.			

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[1] If *gg* contains the kathode, it may be filled with mercury instead of amalgam.

In these results the resistance, after attaining a constant value, decreases by about 1 per cent when the load is added. It can not, however, be affirmed with certainty that this decrement is the true electrical effect of the stress increment. All I have done is to narrow down its value to the order of 1 per cent.

62. *Data for 185°.*—My next experiment was made with aniline. The apparatus is shown in Fig. 9. Similar parts are lettered as in the preceding figures. The aniline is contained in the boiling tube *d*, *g*. The experimental tube *abc* being tied to the fixed central tube *gg* of the apparatus by a piece of rubber tubing, *m*, it is easy to surround both the inside and outside of *abc* with mercury. Current passes in at *f′* and

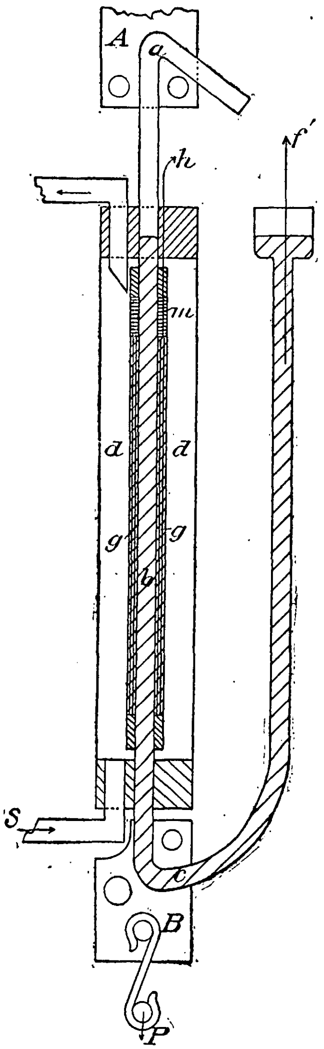

FIG. 8.—Apparatus for testing the viscosity of stressed glass.

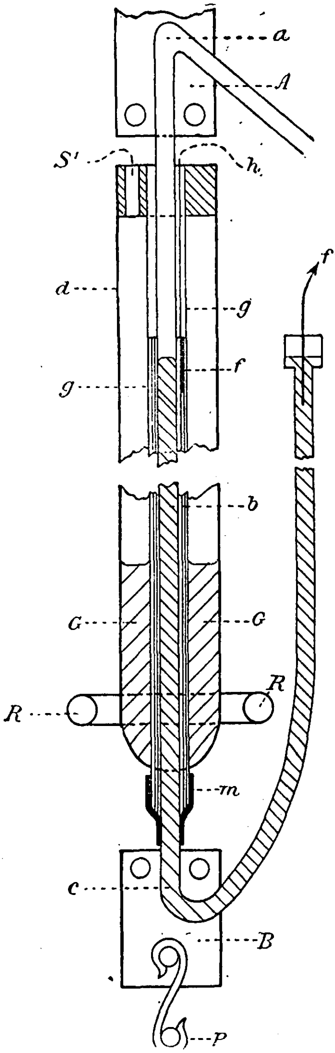

FIG. 9.—Apparatus for testing the viscosity of stressed glass.

out at h. Ebullition is kept up with sufficient intensity to just fill the tube d with aniline vapor, which condenses in the exit tube S', and then runs back. Two Grove cells were found sufficient for the experiment, the observed resistance for this case being about 60,000 ohms.

TABLE 39.—*Resistance of stressed glass.*

[$2\rho_1 = \cdot 53^{cm}$. $2\rho_2 = \cdot 40^{cm}$. $l = 6^{cm}$. $\theta = 180°$.]

Time.	Load.	Deflection.	Time.	Load.	Deflection.
h. m.	*kg.*	*cm.*	*h. m.*	*kg.*	*cm.*
3 21	0	23·6	3 47	10	24·1
23	0	23·7	50	10	24·0
25	4	24·1	51	15	24·0
30	4	24·2	55	15	24·2
31	0	24·0	56	20	24·3
35	0	24·4	60	20	24·1
36	10	25·5	62	0	24·3
40	10	24·2	63	20	24·5
41	0	24·3	67	20	24·3
45	0	24·8	68	21	Breaks.

These results do not certainly indicate any electrical effect of the applied stress at all. They narrow down its possible value to about 1 per cent, thus corroborating the results at 100°.

63. *Results of twisting.*—After making these experiments, the general character of which is negative, but not conclusively so, I made a variety of similar attempts to obtain an electric effect of twisting, but I arrived at no definite results, although I carried the experiments forward to the point of rupture. I omit the data.

64. *Differential apparatus.*—Having these results in hand it appeared probable that the work could be carried to a greater pitch of nicety by comparing strained and unstrained glass simultaneously.

The apparatus with which most of my definite experiments were made are shown in Figs. 10 and 11, and are differential in kind. The resistances across equal parts of the walls of two nearly identical glass tubes, respectively stressed and unstressed, are compared. These tubes are shown at *abcF* and *ekhf*. The ends proper are bent hook-shaped, and those of the glass tube to be operated on, fastened by aid of screws and cement, between slabs of wood A and B. A is fixed; B provided with a hook, P, from which a scale pan may be hung, or with a lever arrangement for twisting. In the experiments made the load was gradually increased as far as 20 kg., but the tubes were strong enough (theoretically) to sustain about three times this weight. The remainder of the figure shows the devices for heating and for passing the currents. Fig. 10 is adapted for high boiling points (aniline, etc.), Fig. 11 for steam. An apparatus similar to Fig. 10 was used for mercury. In Fig. 10, G is the ebullition liquid, heated by a Gibbs's ring burner RR

surrounding the wide glass tube *dd*. A narrower glass tube *gg*, closed below with a perforated cork through which pass the experimental tubes *abc* and *ekh*, is partially filled with sodium amalgam. This is practically one terminal of the battery, the wires connecting at *p*. The other terminal, after passing through the respective coils of a differential galvanometer, connects at *m* and *f* with the sodium amalgam contained in the experimental tubes *abc* and *ekh*.

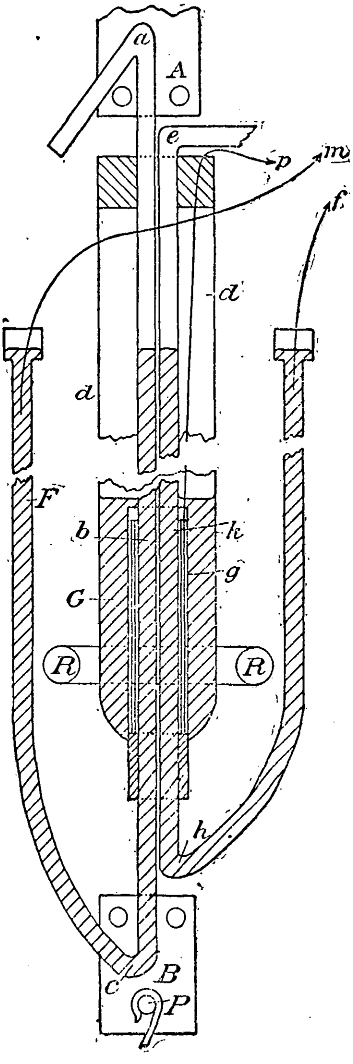

Fig. 10.—Apparatus for 200°.

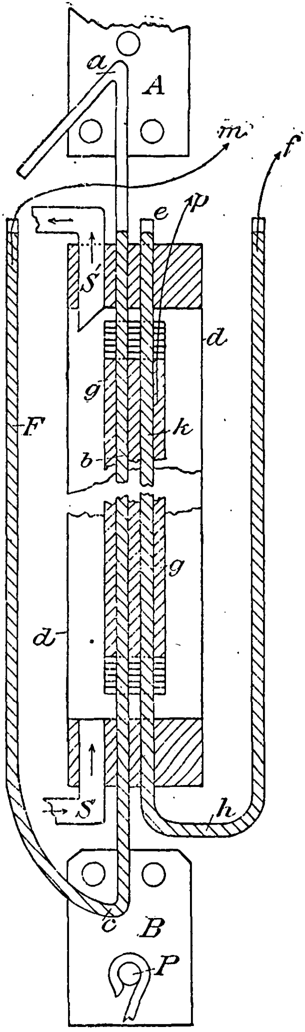

Fig. 11.—Apppparatus for 100°.

The notation in Fig. 11 is the same as that in Fig. 10. The two forms of apparatus are essentially identical, except that in Fig. 11 it is expedient to pass steam through *dd*, the vapor entering at *S* and leaving the apparatus at S'. For reasons stated below, § 67, it is desirable that the menisci of the amalgam contained in *abcF* and *ekhf*, Fig. 10, be visible above the level of the upper cork of the tube *dd*. The amalgam in *gg*, Fig. 10, should be submerged below the level of *G*. Inasmuch as sodium amalgam is necessary only at the anode, ordinary mercury may be used at cathodal parts, and these may therefore be exposed to hot air or steam without annoyances. To summarize: Current arriving at *m* and *f* passes into the sodium amalgam core of the tubes *abc* and *ekh*, thence across the walls of the hot parts of these tubes into the mercury surrounding them, and finally via *p* back to the battery. Regarding other apparatus, cf. § 69.

65. *Results for torsion.*—I commenced work with torsion experiments of which I may indicate something here. A battery of 10 Grove cells was used and the analine at *G*, Fig. 10, kept both below and at the temperature of ebullition. The deflection of each coil alone being $16{\cdot}4^{\text{cm}}$, it was found that the differential action (nearly zero) could not be modified by twisting more than $0{\cdot}02^{\text{cm}}$. Hence the specific electrical effect of twisting can not be greater than about 0·1 per cent. The resistances encountered in these cases were about 200,000 ohms. Profiting by this preliminary experience, however, I was ultimately able to detect and measure the effect of torsion on electrolytic conductivity, using a different and more sensitive method to be indicated below, § 69.

66. *Character of traction effects.*—In case of traction, the data decisively indicated an increase of conductivity proportional to the pull. But this result is necessarily complex in kind, and must be carefully scrutinized before its true signification can be stated. I will therefore give my experiments in chronological order, the first series being made at 185° (aniline), the second at 100° (steam), the third series finally at 360° (mercury).

One remark may be made at the outset: Inasmuch as the electrical effect of traction is persistent with the traction, and is an *increment* of conductivity, it can not be due to temperature. For the extension of an elastic solid like glass[1] produces temporary cooling, § 70.

67. *Results for traction.*—The resistance across the walls of the experimental tube at 190° was about 100,000 ohms. In case of intense ebullition, the temperature is not fully constant. It is therefore desirable to use the apparatus, Fig. 10, just below the boiling point of aniline, and to bring the plane of the ring-burner slightly below the plane of the ebullition liquid *G*. Parts of the apparatus which are not to be heated are screened with asbestos. In this way a nearly stationary distribution of temperature is reached.

Under these circumstances, when a weight of 18 kg. is alternately placed on the scale-pan and removed from it by mechanism, thus subjecting the tube to periodic pulls of the force given, a definite and persistent oscillation of the galvanometer needle ensues synchronously

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[1] Cf. Sir William Thomson's Collected Papers, vol I, p. 308.

with the period of stress. The amount of this oscillation was found to be equivalent to a resistance-decrement of 1,500 ohms for the stressed tube. In other words, the effect of the pull of 18 kg. is a diminution of the resistance of the stressed tube amounting to about 1·4 per cent. These experiments were repeated many times with practically the same results; e. g.:

P = 2 kg., resistance reduced ·4 per cent
P = 15 kg., resistance reduced 1.2 per cent
P = 20 kg., resistance reduced 1·4 per cent

data in which the oscillation of the needle was made the basis of comparison. They betray a somewhat wide margin of error, because glass at 190° is exceedingly sensitive even to trifling changes of temperature. Nevertheless, the data are sufficient for the present purposes, and work of a more precise character with high-temperature vapor-baths seemed to me to be superfluous. By using a more sensitive galvanometer such measurements can be repeated at 100° with facility and much greater precision.

68. *Discussion of these results.*—The result obtained is clearly a superimposed effect, being due in part to the elastic change of dimensions during stretching, and in part to the direct action of stress in promoting molecular break-up. It is therefore necessary to estimate the value of the former influence.

The radii of the tube being $\rho_1 = {\cdot}26^{\mathrm{cm}}$ and $\rho_2 = {\cdot}19^{\mathrm{cm}}$, the section is about $q = {\cdot}1^{\mathrm{cm}^2}$. Supposing the tenacity of glass to be $6{\cdot}5 \times 10^8$ dynes per square centimeter, this tube should bear 65 kg. Tubes are rarely free from imperfections, such as result from insufficient annealing, and it is moreover difficult to apply traction in an experiment like the present without some flexural or other strain across the section (tendency to be crushed between the slabs *AB* at the supports, for instance). Hence, I found it practically difficult to strain these tubes with more than a pull of about 25 kg. without producing rupture. But from all this it appears clearly that the longitudinal extension produced by 18 kg. is much *below* the maximum for the given dimensions and mean strength of tube.

If the tenacity of glass be $6{\cdot}5 \times 10^8$ and Young's modulus $5{\cdot}5 \times 10^{11}$, the values given by J. D. Everett,[1] then the maximum longitudinal extension is ·0012. Again, since Poisson's ratio for glass is nearly $\frac{1}{4}$, it follows that the corresponding radial contraction is about ·0003.

Finally, the resistance R of a hollow cylinder, of length l, radii ρ_1 and ρ_2, and specific resistance s, to conduction across the walls of the tube is (M being the modulus of Brigg's logarithms):

$$R = \frac{1}{2\pi M}\,\frac{s}{l}\,\log \rho_1/\rho_2 = {\cdot}3665\,\frac{s}{l}\,\log \rho_1/\rho_2 \ldots\ldots\ldots\ldots\ldots (1)$$

To evaluate the resistance effect of elastic change of dimensions, R is

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[1] Everett: Units and Phys. Constants, p. 56. These data are reduced from Rankine's "Rules and Tables," p. 595.

to be regarded as a function of l, ρ_1 and ρ_2. In view of the symmetrical occurrence of the last two variables, and if the simplifying relation $4\delta\rho_1/\rho_1 = 4\delta\rho_2/\rho_2 = \delta l/l$, nearly, it follows that $\delta R'/R = (dR'/dl)\delta l/R + (dR'/d\rho_1)\delta\rho_1/R + (dR'/d\rho_2)\delta\rho_2/R = -\delta l/l$, where the accent has reference to elastic change.

Nevertheless radial contraction enters in case of an apparatus of the form Fig. 10, in which decrease of bore during traction lengthens the column of mercury contained. If λ be the length of this column before stretching, its length during stretching is $\lambda(1+2\delta\rho_1/\rho_1) = \lambda(1+(1/2)\delta l/l)$. Hence, in consequence of elongation of the mercury column, $\delta R''/R = -(\lambda/2l)\delta l/l$, nearly, where l is the length of the hot part of the column. Hence, the elastic discrepancy is

$$(\delta R' + \delta R'')/R = -(1+\lambda/2l)\delta l/l \ldots\ldots\ldots\ldots\ldots (2)$$

In none of my apparatus did λ exceed $2{\cdot}5l$. Moreover, λ is always one shank of a U-tube. Therefore ·003 may be assumed as a decidedly superior limit of the numeric of equation (2).

Hence, in an extremely unfavorable case, the resistance effect due to elastic change of dimension (—·30 per cent) is only about one-fifth of the observed effect of traction (—1·4 per cent) produced by a pull much below the tenacity of glass, the said pull (18 kg.) being certainly not more than one-half the maximum load. These effects are very different, and it follows that the decrement actually observed is principally due to *decreased molecular stability* superinduced by stress. In equation (1), s is therefore the variable which chiefly responds to the action of stress.[1]

To obviate the troublesome occurrence of $\delta R''/R$, the column of mercury in most of my experiments was made so long as to extend far *above* the zone of conduction of the stretched glass tube (see Fig. 10). In the apparatus for steam (Fig. 11) the menisci of the column are advantageously raised quite above the cork. In such a case $\delta R''/\mathrm{R} = 0$, and the elastic discrepancy is simply $-\delta l/l$.

In one respect this reasoning is deficient. It does not take into account the changes of elastic behavior of glass due to the heating to 190°. Tabulated constants for this large interval are not available.[2] Hence special cathetometric measurements must be made. At 190° this is difficult, and for these and the other reasons given above (§ 67), it is expedient to refer to the complete set of measurements at 100°. (§ 69.)

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[1] Put $\rho_1 = \rho + e$ and $\rho_2 = \rho - e$; $\therefore\ \rho_1/\rho_2 = 1 + 2e/\rho$ nearly.
Then

$$\delta R'/R = \frac{dR}{dl}\,\frac{\delta l}{R} + \frac{dR}{de}\,\frac{\delta e}{R} = -\frac{\delta l}{l} - M\frac{\delta e/e}{\left(1+\frac{\rho}{2e}\right)\log \rho_1/\rho_2} \quad \ldots\ldots\ldots (2)$$

Here ρ, the mean radius, is supposed to remain constant, and the effect of traction is therefore an increment of length δl and a decrement of the mean thickness, $2e$, of the walls of the tube. Now, the value of $(dR'/de)\,\delta e/R$ is relatively very small. Hence, $\delta e/e = \delta 2e/2e$, and the radial contraction may be regarded identical. Then the value of $\delta R'/R$ in equation (2) is

$$-\delta R'/R = +{\cdot}0012 + \frac{{\cdot}0003 \times {\cdot}434}{(1+3)\log 1{\cdot}4} = {\cdot}0014$$

Hence the *superior limit* of the resistance effect due to elastic change of dimensions, $\delta R'/R = -.14$ %, not differing materially from the above.

[2] Kohlrausch and F. E. Loomis (Am. Jour. Sci. II, vol. L, p. 350, 1870), give low-temperature data for metals.

69. *Traction at* 100°.—At 100° the results can be made more accurate than the above chiefly for two reasons: In the first place, the temperature is easily obtained absolutely constant; in the second, elastic changes of dimensions can be directly measured with facility. In Table 40 I have given the results obtained with the apparatus (Fig. 11.) The method of measuring these large resistances (glass at 100°) is necessarily chosen more delicate than above. I used a high-resistance Thomson galvanometer, read off by Hallock's short-range telescope, and adjusted for differential work. The needle being practically ballistic in kind, the maximum deflections (swing) obtainable by alternately adding and removing the loads P were used for comparison (method of multiplication.) I then determined the amount of oscillation produced by inserting known resistances into one or the other coil of the differential galvanometer. Knowing the resistance of each tube (mean values) from special and preliminary measurements, I was able to deduce the percentage variation of the resistances of glass across the lines of stress. Table 40 contains four series of these experiments; i. e., two sets of results for each pair of tubes. R, the observed electrical resistance per tube, was found to be about 7,500,000 ohms per tube, of which the external and internal diameters were $2\rho_1 = {\cdot}53^{\mathrm{cm}}$ $2\rho_2 = {\cdot}38^{\mathrm{cm}}$, respectively. The table gives the oscillations for the divers loads P; the corresponding absolute decrement δR of R, and the relative value of this decrement in terms of R.

The amount of variation here given for glass is somewhat smaller than was found at 200° above. In the last case, however, the data are less accurate, and definite statements can not be made. In Table 40 the values for the second apparatus are smaller than for the first, a circumstance obviously depending on the tubes chosen, but which I will also leave without further comment.

TABLE 40.—*Resistance of stretched glass at 100°.*

Tubes.	P	Maximum oscillation.	δR	$10^3 \times \delta R/R$.	Method.
	kg.	*cm.*	*Ohms.*		
I and II	6	1·05	—21000	—2·8	Differential galvanometer.
	10	1·63	—33000	—4·4	
	15	2·20	—44000	—5·8	
	19	2·90	—58000	—7·7	
I and II	6	·87	—17000	—2·2	
	10	1·50	—29000	—3·8	
	15	2·17	—42000	—5·4	
	19	2·91	—56000	—7·3	
III and IV	6	·29	— 6000	— ·9	
	10	·74	—15000	—2·2	
	15	1·05	—21000	—3·1	
III and IV	6	·33	— 7000	—1·0	
	10	·76	—15000	—2·3	
	15	1·11	—22000	—3·3	
IV	5	·56	....	—1·2	Bridge.
	10	1·33	....	—2·8	

This table proves conclusively that, within the given limits of variation, the resistance decrement experienced by glass is proportional to the applied stress. For the given conditions ($2\rho_1=\cdot53^{\mathrm{cm}}2\rho_2=\cdot40^{\mathrm{cm}}$) it is as high as $380/10^6$ per kilo stress, and is not below $210/10^6$ per kilo stress. Since the section $q=\cdot10^{\mathrm{cm}^2}$ nearly, it follows that the mean relative variation of resistance due to stretching is about $30/10^9$ per gram load, per square centimeter of section. Mr. H. Tomlinson,* who investigated the effect of stretching metals, finds that for steel, iron, and brass the total variations are only about $\frac{1}{15}$ as large as this, and of the opposite sign. Cf. §74.

70. *Further results at 100°.*—When the temperature is sufficiently constant, for instance, in the case of a steam bath, experiments may be made with a single tube. Let a bridge adjustment be so arranged that $a/b=r/R$ where r is a known rheostatic resistance and R the resistance of the tube, the current in the galvanometer being nearly zero. Then if $\delta r/r$ produce the same maximum oscillation of the needle as $\delta R/R$, it follows that $\delta r/r=\delta R/R$. An accurate chart or table of $\delta r/r$ considered as a function of the oscillation is therefore first to be constructed by aid of the rheostat. This being in hand, the value of $\delta R/R$ corresponding to any oscillation produced by alternately adding and removing the load on the tube, is given at once. This method may be made very accurate, and I was able to obtain not only traction effects, but torsion effects, as indicated by the following data. Here r is approximately 53,000 ohms, R approximately 5,900,000 ohms. In case of torsion, P denotes the load acting during the alternate twisting and untwisting.

TABLE 41.—*Resistance of stressed glass at 100°.*

Preliminary.		Traction.			Torsion.		
$10^3\times\delta r/r$	Oscillation.	P	Oscillation.	$10^3\times\delta R/R$	P	Oscillation.	$10^3\times\delta R/R$
	cm.	*kg.*	*cm.*		*kg.*	*cm.*	
·76	·35	5	·59	—1·3	0	·22	—·5
1·89	·89	10	1·27	—2·8	5	·29	—·6
3·77	1·63	16	1·86	—4·1	10	·28	—·6

The traction data $\delta R/R$ are numerically larger than in Table 40, and hence lend greater favor to the views just expressed. The torsion data $\delta R/R$ are of the same sign as the traction data. In other words torsion decreases the electrolytic resistance. They are of smaller magnitude than traction data and are independent of the load which the tube sustains, so far as I could follow them.

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*H. Tomlinson: Proc. Roy. Soc., vol. 25, 1876, p. 451; ibid., vol. 26, 1877, p. 401.

TABLE 42.—*Longitudinal extension of the tubes, Table 40.*

Temperature.	Load.	L	$\delta L/L$	
°C.	*kg,*	*cm.*	$10^{-6}\times$	
16°	2	77·53	0	
	6	77·53	0	
	10	77·54	130	
	15	77·55	260	
100°	2	77·58	0	Coefficient of expansion ·000008.
	6	77·58	0	
	10	77·60	260	
	15	77·60	260	
100°	2	77·57	0	
	19	77·59	260	
100°	2	77·57	0	
	19	77·60	390	

71. *Dimensional change due to torsion.*—To interpret the above data, special measurements of extension are necessary. These are given in Table 42. They were made cathetometrically and are not intended to give more than a safe estimate of the elastic effect in question. The glass tube to be examined was surrounded conaxially by a second wide tube of glass, through which steam at 100° continually circulated. Measurements were also made at 16°. L is the length between fiducial marks.

Utilizing these values to obtain a superior limit of the elastic discrepancy in Table 40, it appears that $\delta l/l<$ ·0004 and $\delta\rho/\rho<$ ·0001, these data being the largest obtained for the largest load, 18 kg. Hence by equation (2), $-\delta R'/R<2\cdot5\times\cdot0004=\cdot0010$. In other words the elastic discrepancy is numerically much less than ·1 per cent of R, whereas the corresponding mean value for the traction effect in Table 40 (apparatus with tubes I and II, low menisci) is ·75 per cent. Again for raised menisci (Tables 40 and 41, tubes III and IV), $-\delta/R'/R=\delta l/l=$ ·0004. In this case the corresponding mean value of the traction effect is numerically greater than ·50 per cent. In both instances it may be safely inferred that error introduced by elastic change of dimensions is at most about 1/10 of the decrement of resistance actually observed as the effect of stretching.

72. *Effect of temperature.*—I will make a final consideration here, relative to temperature. The thermal effect of traction is negative; its influence on R must therefore be a resistance increment, i. e., opposite in sign to the effect observed. Nevertheless, it is desirable to obtain some estimate of its value, which will probably be found too small for direct measurement. Since $P=20$ kg. and $\delta L/L<.0004^{\text{cm}}$, the total energy *elastically* potentialized per linear centimeter during stretching is $P\delta L/L<10000$ ergs. Hence, even if all this energy were converted into heat, the increase of temperature resulting in case of the given tubes (section $\cdot 10^{\mathrm{cm}^2}$, density <3, sp. heat $<\cdot 2$) would be about $10^4/240 \times 10^4$; *i. e.*, less than ·005°. This datum is too small to produce serious error even in consideration of the phenomenal sensitiveness of hot glass to temperature variations. Estimating that the resistance of glass decreases several per cent (5 to 20) per degree between 100° and 200°, the thermal discrepancy can not be greater, numerically, than the elastic discrepancy.

73. *Traction at 360°.*—I have now to communicate the data obtained at 360°. This case possesses some points of special interest, because the differential apparatus is itself a battery, the action of which enters in a complex manner. The electrolytes here are the hot glass tubes containing amalgam and surrounded by mercury. The actual apparatus was a simplified form of Fig. 10. Fig. 12 presents a clearer diagram of parts, in which *a* and *b* are the hot glass tubes in question, *E* the battery, and *D* the differential galvanometer. The electrical currents due to *E* are indicated by the *inside* arrows; but these currents are considerably reenforced by the action of the element sodium amalgam/hot glass/mercury, as shown by the arrows crossing the tubes *a* and *b*. The electromotive force of this element is easily found by reversing the action of *E*. In an actual experiment I measured NaHg /hot glass/Hg=1·4 volts, a datum somewhat affected by polarization and depending for its value on the strength of the amalgam and the purity of the mercury.

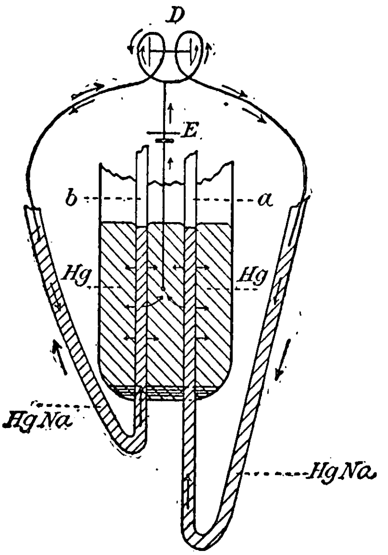

FIG. 12.—Apparatus for 360°.

Besides this large electromotive force there is another of smaller value, due to the fact that the tubes *a* and *b*, with appurtenances, represent two elements switched against each other. The currents are indicated by the *outside* arrows in the diagram, and they are necessarily so circumstanced as not to flow through the galvanometer *G* differentially. Their occurrence is therefore a serious and annoying disturbance, such that measurements at 360° can not, without unreasonable painstaking, be made with the same accuracy as measurements at 100°. I measured the electromotive force in question as about ·2 volt, but it is necessarily variable, even as to sign, containing as it does the polarization inconstancy of both elements.

Since the resistance of glass near 360° is enormously low relative to its value at ordinary temperatures (in some practical cases the apparatus showed less than 1,000 ohms), the extraneous electromotive force *E* can be withdrawn altogether. The present measurements of the electrical effect of traction are therefore made with the NaHg/hot glass/Hg element in the apparatus, Fig. 12, notation being as above, $2\rho_1=\cdot53^{cm}$, $2\rho_2=40^{cm}$. The small resistance at the boiling point is not available; owing to the formation of bubbles at the surface of contact between mercury and glass, the resistance is too variable even for approximate measurement. Hence I observed at a lower temperature, encountering somewhat larger resistances *R*.

Even under favorable conditions these data are only qualitatively satisfactory. They are important, however, because they indicate that at 300° the diminution of resistance due to traction is not larger in numeric value than at 100°; and, since this would be the case if the decrements δR observed were due to elastic change of dimensions, I have here in hand additional evidence against this assumption.

TABLE 43.—*Resistance of stretched glass at 360°.*

Apparatus.	P	Maximum oscillation.	R	δR	$10^3\times\delta R\ R$
	kg.	*cm.*	*Ohms.*	*Ohms.*	
I	6	·50	13000	− 30	—2
	10	·50	....	—30	—2
	15	·70	....	—50	—4
	19	·70	....	—50	—4
III	6	1·00	17000	—15	—1
	10	1·40	....	—22	—1
	15	2·00	....	—31	—2

The present experiments are attended with much annoyance. As the load increases, the tube is apt to break in such a way as to spill the hot mercury; and with all reasonable care several tubes are usually sacrificed before a full series of observations can be obtained.

SUMMARY.

74. The above paragraphs summarized prove that a solid electrolyte like glass is a better conductor of electricity (*i. e.* manifests smaller specific resistance) when in a state of strain (traction torsion) than when free from strain. Inasmuch as the necessary concomitant of conduction in this case is molecular decomposition[1] and recombination, stress of the given kind must promote such decomposition. The rate at which molecular reconstruction occurs per unit of volume increases nearly proportionally to the intensity of stress; and it may in case of traction be carried as far as the limit of rupture of glass amounts to an increment of 1 per cent. In case of torsion the effect is not much larger than about $\frac{1}{10}$ of this, and the increased break-up due to torsion is therefore studied with greater difficulty. The influence of temperature in changing the value of the electrolytic effect of stress is not marked. So far as observed the same pull per unit section does not increase the conductivity of glass more at 350° than at 100°, if indeed it increases it as much.

Again the traction effect in case of electrolytic conduction, being a decrement of resistance, is of the opposite sign of the traction effect in cases of metallic conduction[2] (increment of resistance). The former is also of decidedly greater magnitude. If, therefore, conduction in metals is essentially the same phenomenon[3] as in electrolytes, then the soft metallic state must be singularly well adapted to promote molecular reconstruction. This fine adaptation of structure is destroyed by strains of dilatation, by heat, by alloying,[4] etc. In the data given, the electrical traction-coefficient and the electrical temperature-coefficient (resistance) are similar in sign and in relative magnitude, both in metals and in electrolytes. They are positive in metals and small; negative in electrolytes and large. This is additional evidence in favor of a volume effect discussed at some length elsewhere.

75. *Degree of molecular instability of glass.*—The chief result of the present paper is the emphasis thrown on the fact that, independently of the passage of current, such a solid as glass must be conceived as undergoing spontaneous molecular reconstruction at all temperatures; for, if the reconstruction in question were superinduced by the electric field, then the current passing would vary at a power higher than the first of electromotive force; whereas it may be taken for granted that currents of the intensity of those discussed above pass through glass in accordance with Ohm's law.[5] Recently J. J. Thomson,[6] among many results of his development of the Lagrangian function, investigated an expression for the number of times n, the electric field is discharged at any point, in case of conduction through either metals or electrolytes. If λ be the specific conductivity, K the specific inductive ca-

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[1] It is best to avoid the term dissociation here. The term molecular reconstruction is used in preference.

[2] Mousson: Neue Schweizer. Zeitschr., vol. 15, 1855, p. 33; H. Tomlinson: Proc. Roy. Soc., vol. 25, 1876, p. 451; ibid, vol. 26, 1877, p. 401.

[3] J. J. Thomson: Applications of Dynamics to Physics and Chemistry, 1888, p. 296.

[4] Am. Jour. Sci., vol. 36, 1888, p. 427.

[5] Fitzgerald and Trouton (Rep. Br. Assoc., 1886, p. 312) show that electrolytes obey Ohm's law accurately.

[6] J. J. Thomson: op. cit., p. 299.

pacity of the medium, then $n=2\pi\beta\lambda/K$; where β is a coefficient the value of which is less than unity and depends on the relative time of destruction and existence of the electric field. Accepting provisional values for β and K, Thomson computes a table of values for the superior limit of n, in cases both of metals and of electrolytes. From this table it appears that n for mercury, for instance, is less than 8×10^{15}. Similar values for the limit of n in case of glass at the above temperatures of observation, 100°, 200°, 360°, may be deduced. In round number the specific resistances of glass at the temperatures stated were 10^8, 10^5, and 5×10^3 ohms, respectively. From this it follows nearly that for glass at 100°, $n=8\times10^7$; at 200°, $n=8\times10^9$; at 360°, $n=16\times10^{11}$. Thus it is fair to conclude that at temperatures quite as low as 100° the spontaneous chemical action, i. e. the continuous rearrangement of the molecules of glass, is a pronounced occurrence.

The given value of the frequency of discharge of field, n, may be further expressed in terms of the number of molecules m, which break up per unit of volume, per unit of time, when the number of molecules q per unit of surface, whose disintegration just discharges the field, and the mean distance x, over which they are urged by the field during the interval between break-up and recombination, are known. For $n=mx/q$; or $m=n\ (q/x)$. Here x is a very small quantity, not exceeding the centimeter numeric of the mean free path of the molecule of a gas; whereas q is a very large quantity. Hence m is larger than the given value of n, even if the above superior limits be 100 times the true value of n.

These approximate statistics are the nearest exact statement for the phenomenon of molecular break-up which I can adduce, but they suffice for the present purposes. They show that even when glass is practically an insulator the number of active molecules m considered absolutely is very large and that m need by no means be negligibly small even in comparison with the total number of molecules per unit of volume.

The above paragraphs prove that the rate at which molecular break-up takes place is appreciably greater when glass is under stress than when it is not. It is improbable that the system will instantaneously state of molecular equilibrium to another Hence; pass from one since even in case of very high resistance, such as that of glass at 100°, the number of unstable molecules per unit of volume must still be conceived to be very large, it follows that the species of molecular break-up in question may be looked upon as a fruitful cause of viscous deformation.

CHAPTER IX.

THE ENERGY POTENTIALIZED IN PERMANENT CHANGES OF MOLECULAR CONFIGURATION.

76. *Introductory.*—In the following work a soft annealed wire is stretched by a known weight falling from an initial position (strain minimum) to the lowest position compatible with the given adjustment (strain maximum). If the wire remains sufficiently soft throughout the experiment the recoil is nearly zero. Hence the energy expended in stretching is to this extent easily measurable; and, if also the heat evolved during stretching be measured, the difference between the work done on each centimeter of wire and the heat produced per centimeter of wire is the energy potentialized; i. e., the energy which permanently manifests itself as tensile strain. Using the nomenclature of Maxwell's theory of viscosity, the numerical datum thus obtained is an expression for the amount of change in the history of the typical molecular configuration, the dates being taken immediately before and immediately after the tensile stress is applied.

Now it is clear that the strain effect of a given amount of work done must depend on the dimensions of the material. Strain must be supposed variable with the extension produced in case of a given sectional area, as well as with the section of the stretched wire in case of a given extension. At the outset it is difficult even to conjecture in what respect these strains, though of a given class, may differ in essential details. There is, however, a more interesting phase of these experiments: the strain-effect of a given amount of work done on centimeters of wire will vary, cæteris paribus, with the material acted upon. From this point of view the prosecution of the present research promises to lead to results bearing directly on the nature (form and mutual relations) of the molecules sustaining strain.

77. *Apparatus.*—In Fig. 13 *CC*, *C′ C′*, the weights ($P=30$ kg to 60 kg) by which stretching is to be done are supported on a suitable trap door, *BB*; and the fall of *BB*, when released, is guided by the upright slides *ss*, *s′s′*, fixed in the firm base, *G*, of the apparatus. I took pains to adjust the soft wire *ab* to be acted on as nearly straight and free from initial tensile strain as possible. It was firmly fastened above to a heavy cross-timber of wood, *DD*, the lintel of a framework which in form and purpose closely resembled a gallows. The screw clamp at *a* in the vertically adjustable brass torsion-circle *A*, the axle of which passes snugly through *DD*, secures the upper end of the wire. The lower end is lapped around the hook of the weight pan, *bnn*, then wound around the wire and soldered, care being taken to avoid such loops and kinks as might change form during stretching.

A thermo-couple, $a\beta a\delta$, originally of platinum/platinum-iridium, with its junction β tied on with silk thread on the upper half of the wire *ab*,

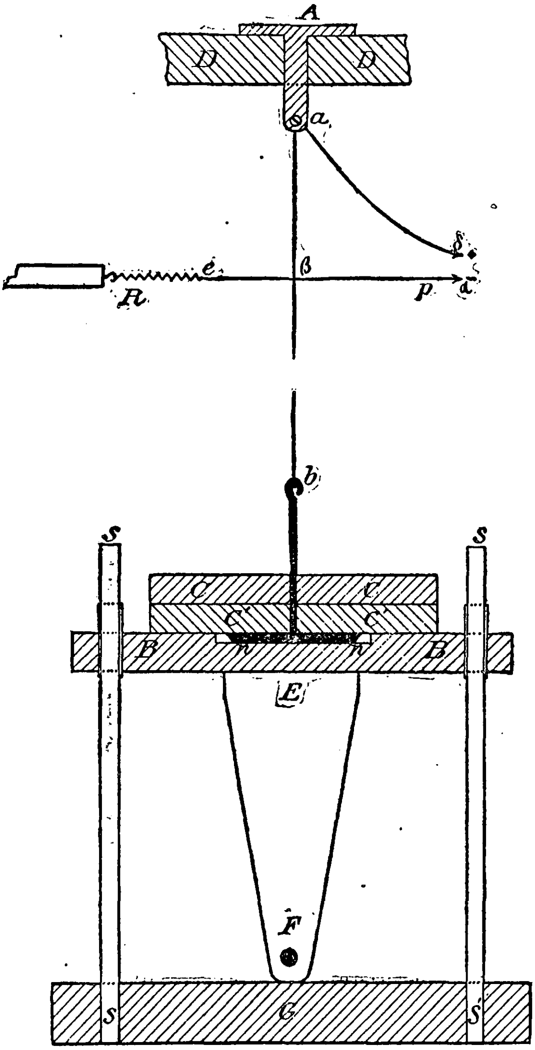

FIG. 13.—Apparatus for measuring the thermal effect of stretching.

enabled me to measure the change of temperature due to stretching. In later experiments more reliable devices were adopted; cf. § 80. Changes of length were measured with Grunow's cathetometer, two fiducial marks having been painted on the wire *ab* about 70^{cm} apart. At a given signal the catch-board *EF* of the trap door *BB* was jerked away, by aid of a rope tied at F and manipulated by an assistant.[1] Simultaneously with the stretching I read off the temperature-increment in terms of the excursion of the needle of a sensitive mirror galvanometer, and as soon as this was taken I made the final length measurement with the cathetometer. From these both δL and δl, i. e., the length-increment of the whole wire and of the part between the fiducial marks, respectively, were derived.

δL varied between 8^{cm} and 20^{cm}, δl between 6^{cm} and 11^{cm}, L being about 120^{cm}.

78. *Results.*—In Table 44 I have systematized the results of the measurements. Here ρ_s and ρ_h denote the radii of the wire before and after straining and are computed from gravimetric measurements. P is the stretching force; $\delta l/l$, the longitudinal extension produced and measured between fiducial marks on the wire with the cathetometer. $E=P\delta L/L=P\delta l/l$ is the work done on centimeter of length; t, the observed increment of the temperature of the wire resulting. Finally, $r=E_t/E$ indicates the part of the applied work which is converted into heat, the remainder $(E-E_t)/E$ being potentialized. The table contains both $P\delta L/L$ and $P\delta l/l$, the latter being usually greater in consequence of errors of experiment which need not here be considered.

The heat corresponding to $t°$ being $Amct$, where A is the mechanical equivalent of the water-gram-degree in ergs, m the mass of the wire per centimeter, and c its specific heat. I was obliged to take c from tables and also for want of data to disregard the variations of c during straining.

TABLE 44.—*Energy potentialized in tensile strains. First method.*

Metal.	$2\rho_s$ $2\rho_h$	P	$\delta l/l$	$P\delta L/L$	$P\delta l,l$	t	$r=E_t/E$
	cm.	*g.*	(*cm*)	*Megalergs.*	*Megalergs.*	°*C*	
Brass	·1662	60,000	·129	7·5	7·7	4·3	0·40
	·1546		·163	9·3	9·8	4·1	·30
			·151	9·0	9·1	3·9	·31
			·168	9·9	10·1	4·3	·31
			·153	9·1	9·2	6·0	·45
			·160	8·9	9·6	7·0	·52
Mean	....	....	·154	8·95	9·24	4·9	·38
Iron	·1362	50,000	·087	4·26	4·35	3·8	0·47
	·1310		·091	4·33	4·56	4·0	·47
			·084	4·17	4·22	4·3	·54
			·087	4·26	4·36	3·5	·43
Mean	....	....	·0875	4·25	4·37	3·9	·48
Copper ...	·1630	40,000	·147	5·58	5·88	6·0	0·77
	·1514		·148	5·51	5·92	5·1	·65
			breaks	....	....	5·5	....
			·153	5·90	6·12	5·3	·65
Mean	....	....	·149	5·66	5·98	5.5	·69

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[1] Mr. Ernest L. Howard had the goodness to give me much efficient service during the course of the present experiments.

In Table 45 I have given the densities of the metals, strained and unstrained, $\varDelta_s$, $\varDelta_h$, and $\varDelta_{hs}$, referring to wires which are soft, strained hard, and softened after straining, respectively. Brass shows a slight decrease of volume after straining; but this result, like that of iron, is doubtless obscured by differences in the composition, hardness, etc., of parts of the annealed wire. Annealing the stretched iron wire scarcely shows any volume effect. In case of copper the effect of stretching is a definite increase of volume of a few tenths per cent. Small as this datum is, it is well to bear in mind that a like expansion of the wire produced by heat, calls for an increase of temperature of 30° or 40°. Elsewhere I have shown that it is scarcely safe to draw conclusions of this kind unless data are in hand in great numbers.

TABLE 45.—*Variation of density of stretched wire.*

Metal.	No.	Δ_s	Δ_h	Δ_{hs}
Brass	I	8·419	8·420	
Brass	II	8·411	8·419	
Iron	I	7·702	7·683	7·686
Iron	II	7·676	7·681	7·681
Copper	I	8·881	8·865	
Copper	II	8·879	8·867	

79. *Discussion of errors.*—A few words on the errors involved are essential. Comparison of the values of $P\delta L/L$ and $P\ l/l$ shows that the work lost upon kinks and flaws, together with that spent upon the framework, is not seriously large so far as the present purposes are concerned. This is also true of the energy elastically potentialized, as may be found by direct tests. The satisfactory measurement of the thermal datum t, however, is much more difficult. Apparently the graduation of the thermocouple is simple, for it is merely necessary to make preliminary observation of the throw of the needle of a ballistic galvanometer produced by given increments of temperature. The use of such graduation is, however, only permissible if the temperature of the wire remains constant during the period of oscillation of the needle. These conditions are never rigorously given; whereas even in case of jacketed wires it is a question whether they are sufficiently given. The temperature of the wire increases very rapidly to a maximum, and then decreases by radiation, etc., reaching the original thermal value in a few minutes. Again the cooling effect of the metallic wires of the thermocouple can not easily be allowed for, neither can it be considered negligible even in case of filamentary wires. Finally the error of heterogeneity is of serious consequence; for the thermoelectric measurement is virtually a thermal exploration of the metal lying very near the point-junction. Hence since the wire near such a point may be imperfect by reason of flaws or composition, so that more or less work is done here than at other parts of the wire, it follows that the temperature thermoelectrically obtained is not a mean datum for the wire taken as a whole.

Unfortunately the combined effect of the errors stated will usually be the cause of too small a value of t. Some assurance of the approximate truth of the results in Table 1 may, however, be obtained by observing that the experiments made are to some extent differential in kind. For instance, cœteris paribus, for an expenditure of only two-thirds the work applied to the brass wire, about the same heat is evolved in the copper and the brass. Sections and thermo-couple are here the same and similarly adjusted.

80. *Successive stretching.*—The importance of the thermal datum is such, however, that special corroborative measurements are essential. To obtain these, the above method was modified in such a way that the wire was stretched successively in equal amounts. One end of it was fixed and the other fastened on the circumference of an iron drum of small radius, $\rho = 0{\cdot}9^{\mathrm{cm}}$. By revolving the latter the wire is stretched and the friction of the axle sufficient to keep it so. I chose successive angles of revolution, π, by which extensions $\delta L/L = {\cdot}054$ each were easily produced and could usually be repeated 4 or 5 times.

These accumulating strains are numbered in Table 46, in the first and second parts of which the data δt are obtained by a $Pt/Pt\text{-}Ir$ thermocouple with wires $0{\cdot}05^{\mathrm{cm}}$ in diameter; in the third part by a filamentary iron / brass thermocouple (wires $0{\cdot}02^{\mathrm{cm}}$ in diam.). Moreover in part I the junctions are fastened by binding them down upon the metal to be stretched by platinum wire. In parts II and III the junctions are bound down with silk, as in Table 44. In part IV the couple is of the kind used in constructing Table 47 below. The data of Tables 44 and 46 when referred to the same value of $\delta L/L$ agree fairly well. Some difference in favor of the silk fastening is apparent. Again δt increases in proportion as the wire is more nearly stretched to the point of breaking. This is in part due to the fact that as the wire hardens more work must be done to stretch it. When the wire breaks (strain V) the resilience is usually sufficient to increase δt appreciably in consequence of the energy elastically potentialized. Finally it is easily seen that, although the mean values of δt in case of the divers metals are not very different, this is not true for the amount of work done in stretching. P varies widely, being less in copper than in brass and less in initial than in final strains.

TABLE 46.—*Successive stretching.*

[$\delta L/L = 0{\cdot}054$ per pull.]

Metal.	Strain.	I.		II.		III.		IV.
		δt	δt	δt	δt	δt	δt	δt
Brass	I	....	0·8	0·6	1·6	1.3	1·0	2·0
	II	1·1	1·0	1·4	2·0	1·6	2·2	2·5
	III	1·3	1·2	1·3	1·9	1·7	2·2	3·5
	IV	2·0	1·2	1·6	2·4	2·1	2·1	3·9
	V	....	1·2	....	2·6	3·0	3·2	....
Iron	I	2·2	2·3					
	II	2·2	2·5					
	III	....	2·9					
	IV	....	2·8					
Copper	I	0·7	....	....	....	....	....	....
	II	1·7	....	....	....	....	....	2·0
	III	2·0	....	....	....	....	....	2·5
	IV	1·8	....	....	....	....	....	4·0

81. *Results of improved methods.*—The errors discussed in § 79 induced me to repeat the work with a thorough change of method, so far as the thermal measurements are concerned. To obtain the data of Table 47, the thick wire *ab*, Fig. 13, was itself used as one of the elements of the thermocouple. The other element was a filamentary wire, $\alpha\beta\varepsilon$, passing from a fixed point, p, in connection with the terminal of the galvanometer, once around the wire to be stretched (junction, β), and thence to an insulated spiral spring R, to keep it tense. At the point, β, where the thin wire lapped around the thick wire, both were carefully brightened and good electrical contact was further insured by stiffening the spring R as much as the thin wire permitted. The upper end a of the wire to be stretched placed in connection with the other terminal δ of the ballistic galvanometer completed the circuit. In this way the heat generated by stretching acts at once at the thermoelectric junction of the thick and the filamentary wire, while the latter may be chosen so thin as to produce only negligible cooling. Indeed, in virtue of friction the discrepancy is apt to be in the opposite direction.

In this arrangement,[1] a special error is introduced by the change of thermoelectric constants due to stretching, but this error, for the present purposes at least, is negligible in comparison with the thermoelectric powers copper/iron or brass/iron, being not greater than a few per cent.

The notation of Table 47 is the same as that in Table 44. E_p, the mean energy stored in the wire per centimeter of length, has been added.

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[1] After making these experiments, I found that a similar method of thermoelectric measurement has recently been employed by Wassmuth (Wiener Sitzber., vol. 92 (2), 1888, p. 52). Wassmuth's purposes are distinct from mine.

TABLE 47.—*Energy potentialized in tensile strains.—Second method.*

Metal.	$2\rho s$ $2\rho h$	P	$\delta l/l$	E	t	E_t/E	E_p
	cm.	*g.*	(*cm.*)	*Megalergs.*	°*C.*		*Megalergs.*
Brass	·166	60,000	·199	11·8	9·1	0·55	5·0
	·155		·191	11·5	9·0	·56	
			·182	10·9	8·8	·58	
Copper ...	·163	40,000	·153	6·12	6·8	0·81	1·3
	·151		·153	6·12	6·1	·72	
			·153	6·12	6·8	·81	
			·143	5·72	6·0	·76	
			·143	5·72	6·3	·80	
Iron	·136	50,000	·084	4·21	4·0	0·51	2·2
	·131		·086	4·28	3·9	·49	
			·089	4·47	4·3	·51	
Iron	·136	40,000	·032	1·26	0·8	0·36	0·9
			·031	1·23	0·5	·22	

A comparison of the results of Table 44 and Table 47 shows that the latter substantiates and emphasizes the results of the former. In Table 47, moreover, the measurements of the effects produced by stretching the same metal are in very much better accord. It is not improbable that the variations of E_t/E for the same metal in Table 2 may be due to actual differences of hardness or composition of the annealed wires.

In case of iron two values of P occur and the metal exhibits striking differences of behavior in the two experiments. It appears that more energy is potentialized during initial than during final stages of strain. For $P=40$ kg, the small value of t is only measurable as a superior limit. Moreover the extension is here so small that the error due to resilience may be 5 per cent.

82. *Summary.*—To summarize: It appears that as much as one-half of the work done in stretching up to the limit of rupture may be stored up permanently; that the amount of work thermally dissipated varies considerably with the metal acted upon, being very large for instance in the case of copper (75 per cent), smaller in case of brass (60 per cent) and of iron (50 per cent); that in case of the same given metal the work done is very largely potentialized during the incipient stages of strain and very largely dissipated during the final stages of strain. When stress of a given kind is applied to different metals, the total amount of energy which can be stored per unit of section, per unit of length up to the limits of rupture, may therefore be looked upon as a molecular constant of the metal. Table 44 shows that in case of a wire about .16$^{\mathrm{cm}}$ thick stretched nearly to the limits of rupture, at least 5 megalergs per centimeter will have been stored in case of brass and about 1 megalergs per centimeter in case of copper. In iron ·14$^{\mathrm{cm}}$ thick at least 2 megalergs per centimeter are potentialized under the same conditions.

Perusing the present chapter as a whole it will be seen that the experiments made are closely analogous to the usual mode of thermochemical measurement. The difference between the initial and the final energy of a system of two interacting liquids is the heat evolved during mixing. In solid metals this experiment can be made with a single substance. The reactions are such that energy is absorbed during straining; in other words the difference between the final and the initial energy of the system of weight and wire is the heat evolved in stretching. It does not follow, however, that the increased intrinsic energy of the strained metal occurs in consequence of the formation of new molecules of greater intrinsic energy; for the added energy may be stored in modified systems of the original molecules. Nevertheless it is interesting to note that the diminished viscosity which usually results from permanent strain corresponds to an increment of the intrinsic energy. Viscous motion is therefore the result of the tendency of the increment of energy to dissipate, since the systems within which it is stored are unstable.

CHAPTER X.

THE CHEMICAL EQUILIBRIUM OF SOLIDS, IN ITS RELATION TO PRESSURE AND TO TEMPERATURE.

EARLIER RESEARCHES.

83. In a recent number of the American Journal[1] I communicated certain data on the effect of dilatational strain on the electric resistance of glass. These experiments, though decisive as to results, were somewhat complex in character; and from their important bearing on the chemical equilibrium of solids, I resolved to attack the subject from a new point of view. The present work is direct, and I hoped that results could thus be reached without necessitating auxiliary hypotheses or experiments. In this expectation I deceived myself: the insulating oil which transmits pressure to glass shows a pressure-coefficient usually much larger than the glass itself. Both must therefore be studied. Nevertheless the confirmation of my earlier results which the present paper gives is gratifying. I am thus able to carry the deductions one step further. Again, the behavior of liquid hydrocarbon insulators under pressure presents many points of special interest in relation to the formation and occurrence of ions.

As a result of the investigation of different oils, I have been able to increase the efficiency of my screw-compressor[2] in marked degree. By using a sticky *mineral* machine oil, thick enough to be almost opaquely fluorescent[3], not only does the screw of my apparatus run more easily, but leaks at high pressure are practically absent. Moreover, the gasket of marine glue is not in any measure dissolved (this is the case with sperm oil), and it therefore lasts indefinitely. Finally, the insulation of barrel and piezometer is now at least as high as 10,000 megohms and need not be less than 1,000 megohms. This is an important requisite in experiments like the present.

The special work on the effect of pressure on the electromotive force of the cell NaHg/glass/Hg has intrinsic interest apart from its subsidiary purpose as embodied in the present text. From experiments to be published in a bulletin of the U. S. Geological Survey, I infer that the secret of the relation of the Peltier contact to the Volta contact will probably manifest itself, if a suitable cell, suitably compressed, be carried through a large range of temperature quite into red heat.

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[1] Am. Jour. Sci., vol. 37, 1889, pp. 339-351.

[2] Phil. Mag., 5th ser., vol. 30, 1890, p. 338.

[3] Possibly containing rubber.

I gain another inference by comparing the present results with the data of my last paper[1] on the effect of pressure on the thermal relations of metallic and electrolytic conductivity.

Finally, the present work is tributary to an extended series of experiments on the relation of melting point and pressure, as will appear in § 88. Thus it forms an essential part of the work suggested by Mr. Clarence King.

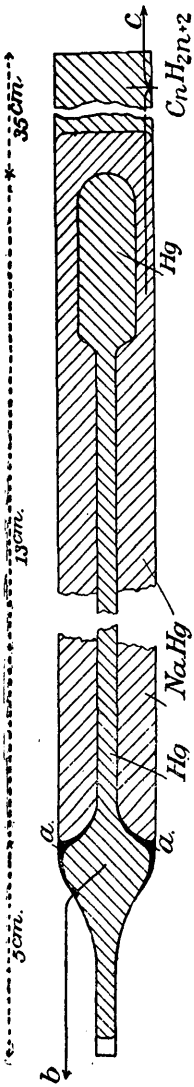

FIG. 14.—Tube for measuring the pressure increments of the electric resistance of glass.

APPARATUS.

84. *Compressor.*—Hydrostatic pressures as high as 1,500 atmospheres were applied. Having found that within the limits of the present paper nothing essentially novel was gained by excessively high values of pressure, I facilitated my work by avoiding them as much as possible.

85. *Vapor baths.*—To obtain different constant temperatures, the tubes were exposed successively to vapors issuing from water (100°), turpentine (160°), naphthalene (215°), and diphenylamine (310°). A serviceable continuous vapor bath for this purpose is also described in the paper last cited. I need only add that the ends of the brazed copper bath are provided with screw stuffing-boxes of the ordinary kind, in which either asbestus packing or a hollow cylinder of cork may be forced home by the gland. Vapor baths must be removed hot. They then slide off the smooth steel piezometer easily, and without jarring the tube.

86. *Insulation.*—In the compressor the arrangement adopted is that of insulating the piezometer tube from the barrel and compression appurtenances. Inasmuch as in some of the experiments the resistances to be measured amount to several hundred megohms, the piezometer insulation must be perfect to at least several thousand megohms. How this was gradually accomplished will be explained in §§ 94 et seq. Gutta-percha covered wire and raised hard-rubber commutators are essential. Care must be taken to insulate the water-jackets which cool the ends of the piezometer, and to allow the efflux water to drop into a cistern discontinuously. The burners which heat the vapor bath must be insulated to prevent conduction through the flame, etc. At high temperatures, where the resistance of the glass will have decreased several hundred to one, many of these precautions are superfluous. They are always necessary when oils are examined.

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[1] Am. Jour. Sci., vol. 40, 1890, pp. 219-222.

87. *The resistance tube.*—The original apparatus for measuring the resistance of compressed glass is shown in Figures 14 and 15, of which the latter is a diagram. Fig. 14 consists essentially of two coaxial glass tubes, the larger completely surrounding the smaller. The diameter of the larger (thick-walled) tube is ·4 to ·5^{cm}; that of the inner (thin-walled) tube is ·2^{cm}. They are joined along the ring *a a*. Two separate compartments are thus formed, the inner of which is filled with pure mercury and the outer with sodium amalgam, to a sufficient length to completely envelop the inner tube. The end of the large tube contains hydrocarbon oil, to protect the amalgam against moisture or air when the tube is not in place, and also to prevent the saponification of sperm oil and to eliminate condensible air when the tube is in place. Mercury and the fluid amalgam are to be introduced by aid of the air-pump, care being taken to boil out all traces of air. The mercury of the inner compartment is in galvanic connection with the platinum wire *b*, which in its turn connects with the piezometer tube. Hence *b* need not be insulated. The amalgam is pierced by the terminal *c*, completely insulated, from the piezometer by the *unbroken length of cold-glass tube* surrounding the wire. To prevent the wire from being pulled out of place during the adjustments, *c* is sealed in the inside of the insulator tube as shown in the figure. This

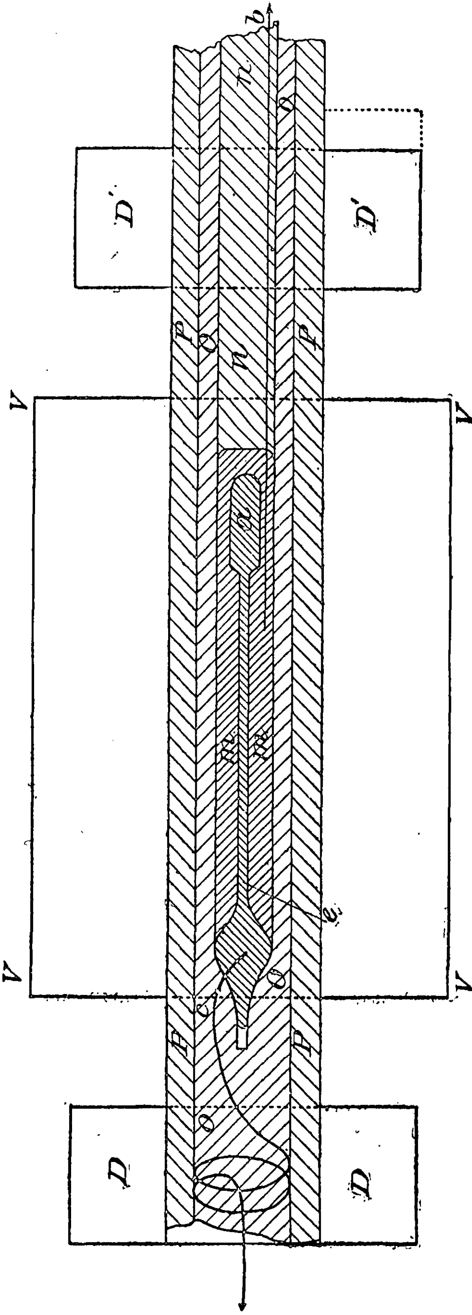

FIG. 15.—Diagram of resistance tube in place.

terminal is in galvanic connection with the barrel. It is seen that the tube is virtually a galvanic cell, NaHg/glass/Hg, and is reversible.

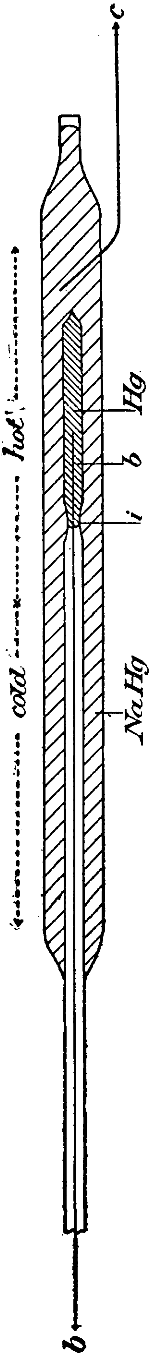

FIG. 16.—Improved form of resistance tube.

Under the influence of hydrostatic pressure the figure of the glass tube is symmetrically reduced in size. Hence, with regard to the conduction taking place across the walls of the *inner* tube, the resistance would be increased, in consequence of changes of dimensions, only by the amount in which the length of the inner tube is diminished. In other words, if $r=sl/2\pi RL$, where s, l, R, L denote respectively specific resistance, thickness, radius, and length of thin tube, then the dimensional effect of pressure is $\delta r=(s'l/2\pi RL)\times\delta L/L$, nearly. But all such values ($\delta L/L$ being less than .1 per cent per 1000 atm.) are negligible in comparison with the relatively large pressure coefficients actually obtained (cf. Tables 48 to 55,) and to be interpreted with reference to $s'-s$.

Fig. 15 (diagram) shows the resistance tube in place. PP is the tubular steel piezometer, surrounded by the vapor-bath V V, and the cold-water jackets D D and D′ D′, and filled with the oil O O, by which the pressure is transmitted. The inner compartment of the glass tube is at *a* (mercury), the outer compartment at *m m* (sodium amalgam), with petroleum at *n n*. The terminal wires are shown at *b* (cathode connecting with the piezometer) and at *c* (anode, insulated).

88. In the course of my work, however, I found it essential to connect *c* with the piezometer and to insulate *b*; for by thus reversing the tube there is no tendency of short-circuiting through oil and the *outer* tube. Indeed, so important is this adjustment, that I further modified the tube, Fig. 13, in the way indicated in Fig. 16.

Here the inner compartment is filled with mercury to only about 7^{cm} of the end. The remainder of the tube, containing hydrocarbon oil, runs completely through the piezometer into the barrel, with which the insulated platinum terminal connects. To keep the mercury in place, the inner tube is drawn down to a smaller diameter (see *i*, Fig. 3), into which the mercury meniscus projects. Air is excluded by boiling the mercury with the platinum wire in place. The latter amalgamates externally, but careful handling is none the less advisable. The outer tube, with its filling of sodium amalgam, not only envelops the inner mercury thread, but extends in both directions as far as the *cold* parts of the surrounding piezometer tube. Since *c* connects with this, no current will pass through the film of *hot* oil and the outer glass tube. All currents between piezometer and barrel must therefore pass through the walls of the inner glass tube—a condition which is further insured by making NaHg/glass/Hg the acting electromotive force. I have purposely described these precautions at length; and their importance is obvious when it is remembered that the oil medium has a larger pressure coefficient than glass, and that the insulation of oil sometimes breaks down in marked degree with rise of temperature (§ 103). The effect of cold oil can be found preliminarily, when the whole apparatus is cold.

89. *Arrangement for testing insulation.*—I have finally to show the apparatus for testing the resistance and pressure coefficient of the liquid insulators at different temperatures. This is given in Fig. 17 (diagram), and consists essentially of a cylindrical steel rod *s s*, adjusted coaxially with the steel piezometer P P, containing the oil to be tested. Tubes of glass, *g g*, hold the rod *s s* in position. Owing to the fact that above 200° glass conducts better than most hydrocarbon oils, this insulating arrangement is not quite satisfactory; but by using thin-walled glass tubes filled with the oil, the data so obtained are sufficient for the purposes of the present text, since the rate of breakdown with temperature is accentuated. It is seen that the measuring current passes from the piezometer P P, through the cylindrical layer of oil, into the rod *s s*, and thence to the battery. The diameters of steel core and piezometer tube being ·13 and ·63 centim. respectively, and the exposed part 9 centim. long, the specific resistance of the layer of oil is easily computed (§ 103).

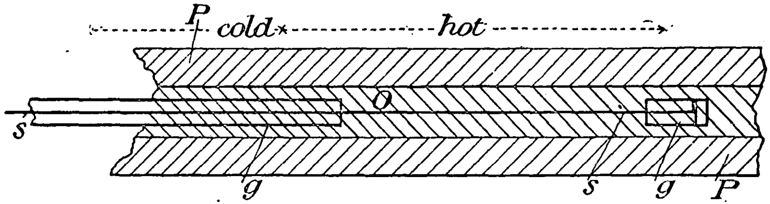

FIG. 17.—Arrangement for measuring the pressure increments of the electric resistance of liquid insulators.

90. *Digression.*—By filling the greater part of the closed end of the inner tube (Fig. 13 or Fig. 14) with the substance to be examined, and the open end as far as *e* with mercury, the tube is available for the study of melting point and pressure. In such a case the forward motion of the inner mercury meniscus due to pressure proportionately decreases the resistance of the arrangement by increasing the opposed surfaces of mercury and sodium amalgam. Increased delicacy is secured by enlarging the bulb at the end of the inner tube. At the solidifying point the sample usually undergoes a phenomenal reduction of volume, corresponding, therefore, to a similarly large reduction of resistance. This occurrence I propose to use as the criterion of solidifying point and of melting point. The apparatus is available above 100° under any pressure up to several thousand atmospheres.

The criterion specified is also available when a fine platinum wire is stretched through contiguous coaxial columns of the substance and of mercury in a vertical piezometer.

91. *Resistance measurement.*—Resistances were first measured by a bridge method; but owing to the fact that electromotive forces are involved which may themselves vary with pressure, I lost faith in the safety of these methods and replaced them by simple circuit methods. The errors to be guarded against are primarily in the experiment itself. Again, the resistance tube (Figs. 14–16) is well adapted for simple circuit work, since the electromotive force NaHg/glass/Hg may exceed a volt, and the only pronounced resistance is in the cell. Only at 100° need auxiliary cells be inserted.

Throughout the work the low-pressure or fiducial resistance is measured *before* and *after* the high-pressure resistance. This safeguard is necessary. From three to five minutes were allowed for the elimination of thermal discrepancies. The fiducial resistance is to be measured under a pressure of 100 to 200 atmospheres, both to condense the air retained in the pump and to make the oil less compressible (§ 116). Not much care was taken in measuring the absolute resistances, since the inferences of this paper are to be drawn from the increments.

92. *Galvanometer.*—In the high-resistance experiments I used the Elliott square pattern of Thomson's high-resistance astatic galvanometer. The readings, however, were made by Poggendorff's method of telescope and scale. To adapt Thomson's concave-mirror adjustment to this purpose, I compensated the curvature by an ordinary "No. 36" concave spectacle glass fixed in front of the mirror, diffuse light being suitably screened off. Glass "No. 36" slightly undercompensates the mirror, leaving some magnification which is not undesirable. How far a weak telescope may be made to do the service of a more powerful instrument, by virtue of the concave mirror and a lens even weaker than No. 36, remains to be seen. With the above adjustment of lens and mirror, using a telescope magnifying somewhat over 20 diameters, and a scale somewhat further than 2 meters from the mirror, I obtained an image about 4·5 centim. long and sufficiently distinct for all practical purposes. Thus, if one volt act in one million megohms, the current produced would only just escape detection.

At 200° the galvanometer was suitably shunted.

93. *Other adjustments.*—Regarding other manipulations, the paper cited in § 84 will have to be consulted. Electromotive forces were measured by a zero method.

OBSERVATIONS.

94. *Tables explained.*—Table 48 contains data for the apparent change of the resistance of glass with pressure, when the liquid which transmits pressure is ordinary saponifiable sperm oil. Here θ denotes the temperature of the vapor bath, approximately, and R the resistance of the uncompressed glass shell. δR/R is the *increment* of resistance, R corresponding to the pressure increment δp, where the initial pressure is at least 50 atmospheres (§ 91). $k_r = \delta\mathrm{R}/\mathrm{R}.\delta p$ is the pressure coefficient. To save space, I have taken the mean of the two or three complete triplet observations for each δp given. The table contains six independent series of experiments, made at different times and often with different tubes. The adjustment, however, was in the main that of Fig. 15 reversed.

TABLE 48.—*Apparent effect of pressure (in atmospheres) on the resistance of glass, in an insulating medium of animal sperm oil.*

Series No. θ R Mean $k_r \times 10^6$	$10^3\times$ δR/R	δp	$10^6 \times k_r$	Series No. θ R Mean $k_r \times 10^6$	$10^3\times$ δR/R	δp	$10^6 \times k_r$
I.	82	470	174	III.	51	480	110
215°.	160	835	193	310°.	99	877	113
$117\times10^3\omega$	213	1180	181	—	165	1320	125
182.				116.			
I.	75	455	167	IV.	164	450	365
215°.	157	825	191	100°.	330	930	355
$117\times10^3\omega$	217	1160	188	—			
182.				360.			
I.	59	497	119	IV.	112	515	217
310°.	117	830	142	160°.	102	525	196
$6\times10^3\omega$	170	1175	145	—	111	610	185
137.				200.			
I.	61	470	130	VI.	420	605	685
310°.	116	845	136	100°.	420	650	640
$6\times10^3\omega$	158	1155	137	—			
134.				660.			
II.	67	390	171	VI.	127	655	194
215°.	135	750	180	160°.	136	644	211
$122\times10^3\omega$	195	1070	182	—	141	674	209
178.				203.			
II.	49	450	112	VI.	126	657	192
310°.	97	790	122	215°.	123	691	177
$9\times10^3\omega$	145	1120	127	—	127	688	184
121.				184.			
III.	85	516	163	VI.	97	689	143
215°.	165	1000	163	310°.	89	639	138
$130\times10^3\omega$	219	1405	156	$10^4\omega$			
161.				140.			

95. *Remarks on the table.*—A graphic construction shows the character of these divers series to be identical, though the individual pressure coefficients show marked variation. The data of the third series are made in connection with the following data of Table 49, in which electromotive forces are measured before and after the resistance measurements. As a rule, the galvanometer needle does not reach its position of equilibrium at once; the slow changes registered are probably due to gradually vanishing thermal discrepancies (§ 121).

96. *Electromotive force.*—Table 49 gives results for the effect of pressure on the electromotive force NaHg/glass/Hg. Here θ is the temperature of the vapor bath, and e the observed electromotive force, in volts, corresponding to the pressure δp, when the initial pressure is above 50 atmospheres (§ 94). $k_e = \delta e / e \,.\, \delta p$ is the pressure coefficient. Five minutes were allowed per observation. Special experiments showed that e decreases on cooling. The medium for transmitting pressure is again ordinary animal sperm oil. Earlier observations were discarded, and the results are condensed as far as possible.

TABLE 49.—*Apparent effect of pressure on the electromotive force of NaHg/glass/Hg.*

θ Mean $k_e \times 10^6$	δp	$e \times 10^4$	$10^6 \times k'_e$	θ Mean $k_e \times 10^6$	δp	$e \times 10^4$	$10^6 k_e$
100°.	0	5180	—	†215°.	0	11182	—
230.	720	5950	210	10·9	488	11244	11·3
	0	4300	—		0	11210	—
	1080	5440	245		992	11332	11·0
*215°.	0	10872	—		0	11224	—
7·3.	533	10904	5·5		1378	11374	9·7
	0	10912	—		0	11214	—
	524	10950	6·7		550	11286	11·7
	0	10922	—	310°.	0	10658	—
	551	10968	7·7	5·1.	505	10672	2·5
	1010	10996	6·8		0	10666	—
	0	10924	—		480	10706	7·8
	535	10976	8·9				
	1011	11008	7·7				
	0	10924	—				
	542	10972	8·2				
	1033	11004	7·2				
	1441	11024	6·5				
	0	10912	—				
	540	10968	9·6				
	1027	11004	8·3				
	1436	11028	7·4				

* Before the resistance measurements.
† After the resistance measurements.

97. *Remarks on the table.*—To facilitate measurement, the greater number of experiments are made at 215°. Polarization was observed; and for this reason the measurement of temperature coefficients by removing and readjusting vapor baths was not tried. The increment of electromotive force is largest immediately after compression (temporary effect), and then decreases to the apparently constant values of the table. The converse holds for the decrement on removing pressure. At 100° no satisfactory results could be obtained (§ 118). At 310°, although the temporary effects were distinct, the permanent effects are not warranted.

98. *Pressure coefficient of sperm oil.*—Table 50 contains results, given on a plan identical with that of Table 48, for the case in which the glass tube (Fig. 14) was removed and the steel rod (Fig. 17) inserted. In this way the pressure coefficient of ordinary sperm oil was found. Table 50 also contains results for glass made after the work with oil.

These results are shown in Fig. 18, where little circles distinguish the observations for oil.

The pressure coefficient of sperm oil is therefore decidedly larger, and the specific resistance of this oil is usually smaller, than that of glass (cf. § 103, Tables 56 and 57); but the breakdown of resistance with rise of temperature is more marked in the latter case. Nevertheless the data of Table 50 cast grave doubt on the trustworthiness of the data of Table 48; and hence a search must be made for more highly insulating liquids. For obvious reasons I selected the hydrocarbon oils of the paraffin series.

99. *Pressure coefficient of gasoline.*—Table 51 contains data for the insulation and pressure coefficient of very volatile gasoline.

These results are shown in Fig. 19.

The resistance of gasoline is therefore enormous as compared with sperm oil, and above 100° more than 100 times that of glass. More-

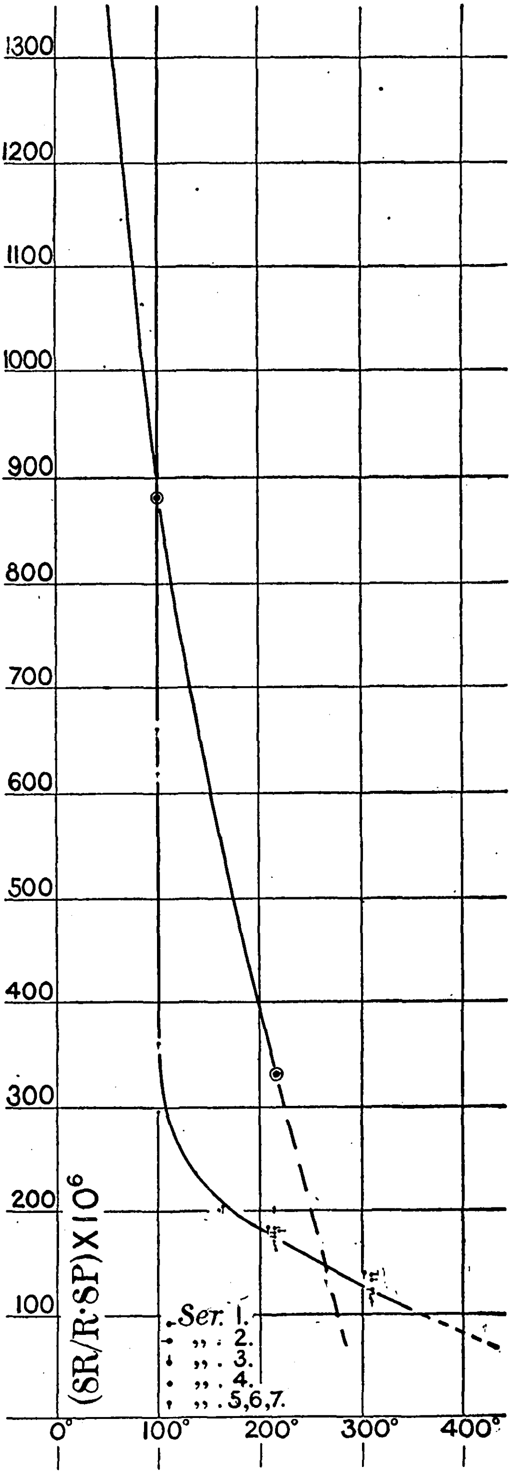

FIG. 18.—Pressure coefficient and temperature for sperm oil and for glass.

over the breakdown of the gasoline insulation with temperature is remarkably slow; but owing to the difficulty of keeping the apparatus free from leaks in the case of this very thin oil, I did not make experiments with the glass tube.

TABLE 50.—*The insulation and pressure coefficient of sperm oil.*

[$p_0 = 100$ atm. Pressure coefficient of glass.]

Series No. θ R Mean $10^6 \times k_r$	$10^3 \times$ $\delta R, R$	δp	$10^6 \times k_r$	Series No. θ R Mean $10^6 \times k_r$	$10^3 \times$ $\delta R/R$	δp	$10^6 \times k_r$
1.	3300	540	6200	Glass tube inserted.			
20°.	3500	573	6100				
$18 \times 10^6 \omega$	8100	1240	6500	VII.	347	570	600
$\times 5700$.	6500	1140	5700	100°.	373	580	640
	2200	553	4000	$240 \times 10^6 \omega$			
				620.			
1.	500	550	910				
100°.	550	610	890	VII.	90	570	157
$2 \times 10^6 \omega$	990	1150	860	215°.	94	560	170
+880	460	550	840	$500 \times 10^3 \omega$	186	1000	186
				171.			
1.	180	550	330				
215°.	200	600	330				
$300 \times 10^3 \omega$	230	675	340				
+330.							

A feature of these results is the negative pressure coefficients found, which themselves decrease algebraically nearly proportionally to the temperature of the oil. At a given temperature the resistance is not constant, but decreases; and since the gasoline is discolored when removed from the press, the decrease of resistance is undoubtedly a solution phenomenon. Indeed, I suspect that negative coefficients are possibly to be associated with solution (§ 123).

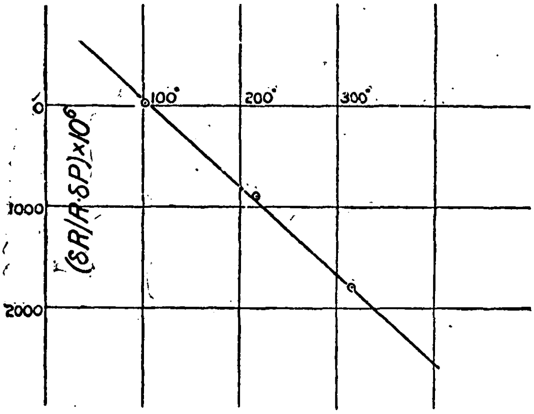

FIG. 19.—Pressure coefficient and temperature for gasoline.

100. *Pressure coefficient of petroleum.*—In Table 52 data are given for ordinary illuminating oil (petroleum). The glass tube still has the form of Fig. 14, reversed. Two sets of experiments were made.

TABLE 51.—*Behavior of gasoline under pressure.*

[Initial pressure, $p_0=200$ atm. Resistance at 20°, $2\times10^9\omega$.]

Series No. θ R Mean $k_r\times10^6$	$10^3\times$ $\delta R/R$	δp	$10^6\times k_r$	Series No. θ R Mean $k_r\times10^6$	$10^3\times$ $\delta R/R$	δp	$10^6\times k_r$
2.	0	250	0	2.	—380	250	—1500
100°.				310°.	—550	300	—1800
$450\times10^6\omega$				$220\times10^6\omega$	—580	300	—1900
to				—1800.	—550	300	—1800
$130\times10^6\omega$					—590	300	—2000
± 0.							
2.							
215°	—330	250	—1300				
$220\times10^6\omega$	—290	280	—1050				
to	—200	280	— 710				
$150\times10^6\omega$	—140	220	— 640				
—890.	—190	250	— 760				

TABLE 52.—*Insulation of pressure coefficient of petroleum.*

[Initial pressure, $p_0=50$ atm. Pressure coefficient of glass.]

Series No. θ R Mean $k_r\times10^6$	$10^3\times$ $\delta R/R$	δp	$10^6\times k_r$
3.	700	460	1530
20°.	700	480	1460
$370\times10^6\omega$			
+1500.			
3.	520	580	890
100°.	570	760	750
$130\times10^6\omega$			
+820.			
3.	134	570	234
215°.	167	590	282
$40\times10^6\omega$	177	580	306
+274.			
3.	—285	550	—521
310°.	—281	570	—492
$47\times10^6\omega$	—229	570	—404
to	—223	640	—349
$34\times10^6\omega$	—192	520	—369
—430.			

Series No. θ R Mean $k_r\times10^6$	$10^3\times$ $\delta R/R$	δp	$10^6\times k_r$
Petroleum tested again. $p_0=200$ atm.			
4.	560	370	1500
100°.	750	360	2100
$740\times10^6\omega$			
+1800.			
4.	115	310	380
215°.	193	305	640
$64\times10^6\omega$	166	300	553
+560.	200	300	667
4.	—115	300	—383
310°.	—175	550	—320
$32\times10^6\omega$	—100	285	—360
—340.	—105	290	—360
	—140	523	—270
	—115	298	—383
	—130	495	—265
	—105	280	—380

Glass tube inserted.

Series No. θ R Mean $k_r\times10^6$	$10^3\times$ $\delta R/R$	δp	$10^6\times k_r$	Series No. θ R Mean $k_r\times10^6$	$10^3\times$ $\delta R/R$	δp	$10^6\times k_r$
VIII.	630	570	880	IX.	400	300	1330
100°.	420	610	680	100°.			
$230\times10^6\omega$				$10^9\omega$			
+780.				+1330.			
VIII.	84	630	132	IX.	20	300	66
215°.	86	600	142	215°.	25	280	88
$200\times10^3\omega$				$700\times10^3\omega$	36	300	120
+136.				+93.	30	300	100
VIII.	20	740	26	IX.	— 25	300	— 83
310°.	34	725	34	310°.	— 32	300	—107
$50\times10^3\omega$	33	665	50	$140\times10^3\omega$	— 17	300	— 55
×43.	40	640	63	—76.			

These results are shown in Fig. 20.

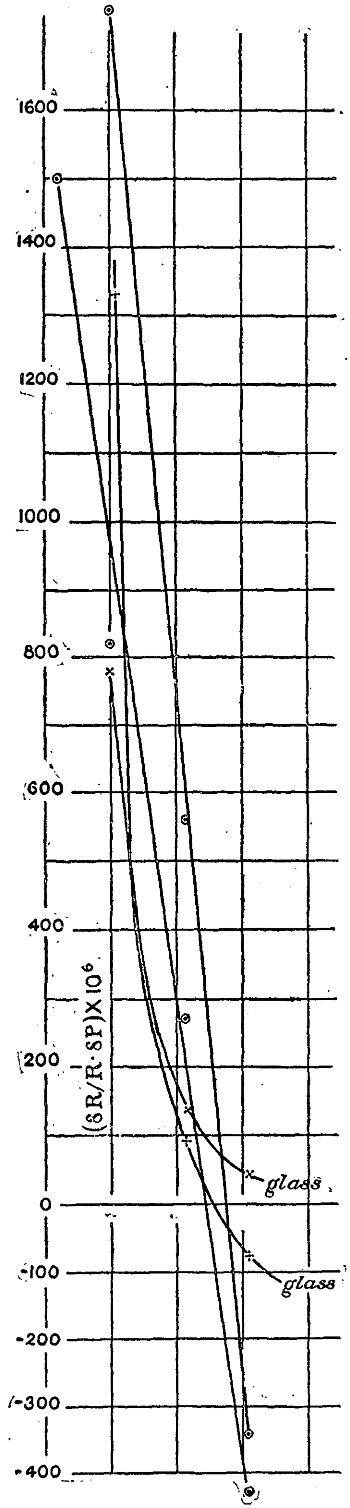

Fig. 20.—Pressure coefficient and temperature for petroleum and for glass.

The specific resistance of petroleum is not so high as that of gasoline, though it is more than twenty times that of glass at 215°, and the insulation breaks down less rapidly. The pressure coefficients decrease in marked degree with rise of temperature and nearly proportionally to it, and they actually pass from positive to negative values. They are of a larger order of numerical magnitude than the glass coefficients. At 310°, where the petroleum coefficient is negative and the glass coefficient, according to Tables 48 and 50, positive, a criterion of the effect of the oil is obtainable. The glass tube[1] does not stand this test fully, since the pressure coefficients of oil and glass in series IX are both negative, though the effect of the glass is a decided algebraic increase of the oil coefficient. Moreover, as the trustworthiness of a tube like Fig. 14 reversed is no longer vouched for, I made the remaining experiments with the tube Fig. 16. I also tested a better insulating oil.

101. *Pressure coefficient of thin machine oil.*—Tables 53 and 54 contain data for the insulation and resistance of thin mineral machine oil ("mineral sperm"), and also for glass surrounded by it. At 215° the resistance of the liquid is more than 50 times that of glass, and the breakdown in the former case much less rapid. Two glass tubes of the form Fig. 16 were used consecutively. In the first of these the internal and external diameters of the inner tube were 0·24 and

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[1] I strongly suspect that some oil had worked itself down into the sodium amalgam, and that this is the true cause of the exceptional behavior referred to in the text. This inference was sustained by a dissection of the tube after the experiment.

0.34 centimeters, respectively; in the other the dimensions of the inner tube were those given in § 87.

TABLE 53.—*Insulation and pressure coefficient of thin mineral machine oil.*

[p_0=150 atm. Insulation at 20°, $3\times10^7\omega$.]

Series No. θ R Mean $k_r\times10^6$	$\times10^3$ $\delta R/R$	δp	$k_r\times10^6$	Series No. θ R Mean $k_r\times10^6$	$10^3\times$ $\delta R/R$	δp	$k_r\times10^6$
5.	400	410	970	5.	95	370	+260
215°.	400	420	960	† 310°.	95	340	280
$320\times10^6\omega$				$50\times10^6\omega$	140	400	350
+960.				+300.	125	390	320
5.	−220	410	−525		400	410	970
*215.	−160	430	−370		400	420	960
$110\times10^6\omega$	−190	440	−430				
−440.							

* Dirty, after an explosion. † Clean, refilled.

TABLE 54.—*Pressure coefficient of glass, surrounded by mineral machine oil.*

[$p_0=150$ atm.]

Series No. θ R Mean $k_r\times10^6$	$10^3\times$ $\delta R/R$	δp	$k_r\times10^6$	Series No. θ R Mean $k_r\times10^6$	$10^3\times$ $\delta R/R$	δp	$k_r\times10^6$
XI.	61	445	137	XI.	57	400	143
215°.	59	420	140	215°.	59	400	147
$80\times10^3\omega$				$190\times10^3\omega$			
+138.				+145.			
XI.	53	425	127	XI.	71	385	185
215°.	67	420	157	100°.	94	365	260
$120\times10^3\omega$				$30\times10^6\omega$	113	375	300
+143				+250.			
XI.	41	363	115	*XII.	66	395	170
310°.	48	415	116	215°.	69	395	175
{ $6\times10^3\omega$ to	46	420	112	$360\times10^3\omega$	63	355	175
{ $8\times10^3\omega$	52	410	126	+173.			
+117.	49	420	117				
	48	415	115	*XII.	54	350	155
				310°	60	350	170
				$26\times10^3\omega$	67	380	180
				+168.			

*Another tube of higher resistance.

Some of these results are shown in Fig. 21.

Repetitions of this work led to virtually the same uniformity of result, as is well evidenced by the close coincidence of the data for 215°. The coefficients of the two tubes, however, are not identical. A feature of Table 53 is the change of sign of the pressure coefficient when the oil has become contaminated. It is in these experiments (Table 53) that I specially observed the apparent accommodation detailed in § 121. As a whole, the data are in reasonable conformity with Table 48.

102. *Pressure coefficient of thick machine oil.*—My final experiments were made with a very sticky *mineral* machine-oil (cf. § 83). Two tubes of the form Fig. 16, but of different resistances, were used (§ 101).

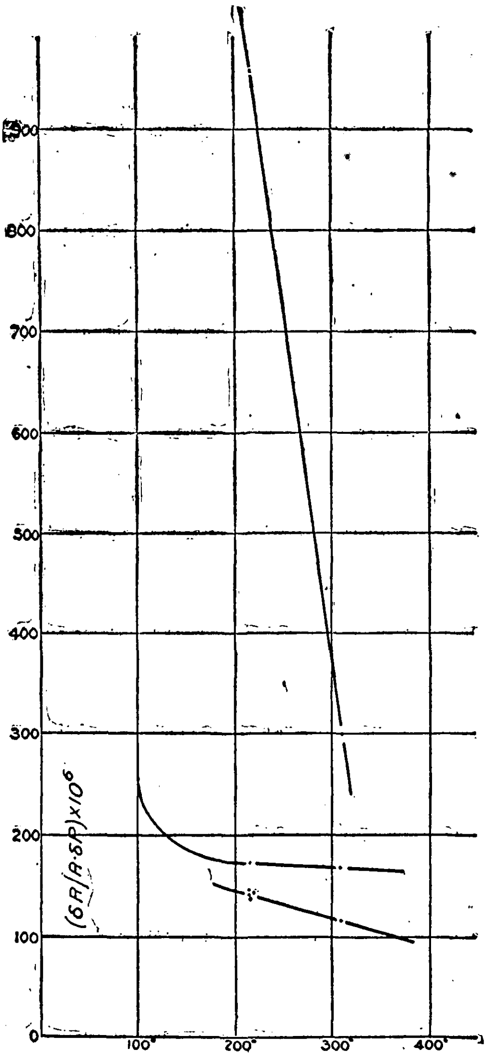

FIG. 21.—Pressure coefficient and temperature for thin mineral machine oil and for glass.

At 310° the oil coefficients are negative, whereas the glass coefficients remain distinctly positive. This seems to be a conclusive test, since an effect of the glass in changing the sign, or in anyway increasing the oil coefficients is inconceivable. The increase of the latter with pressure at 215° (cf. Table 55) is probably an actual occurrence. The two tubes again differ in their properties.

TABLE 55.—*Insulation and pressure coefficient of sticky mineral machine oil.*

[p_0=150 atm. Pressure coefficient of glass. Oil insulation at 100°, $4\times10^9\omega$.]

Series No. θ R Mean $k_r\times10^6$	$10^3\times$ $\delta R/R$	δp	$k_r\times10^6$	Series No. θ R Mean $k_r\times10^6$	$10^3\times$ $\delta R/R$	δp	$k_r\times10^6$
6.	530	810	655	XIII.	73	430	170
215°.	520	820	635	*215.	42	450	92
$130\times10^6\omega$	125	360	350	$120\times10^3\omega$	50	400	125
+510.	155	400	390	129.	Tube broken.		
6.	−140	440	−320	Tube of high resistance inserted.			
310°.	−145	410	−355				
$18\times10^6\omega$	−120	420	−285	XIV.	81	400	202
−296.	−125	450	−280	215°.	84	420	200
	−125	470	−265	$730\times10^3\omega$	165	830	200
	−115	430	−270	+205.	180	830	220
Tube of low resistance inserted.				XIV.	70	415	170
XIII.	52	415	125	310°.	60	420	145
100°.	64	420	150	$36\times10^3\omega$	130	.820	160
$11\times10^6\omega$	115	820	140	+155.	125	780	160
+135.	99	810	125		54	400	135

* Dirty after an explosion.

These results are shown in Fig. 22.

103. *Digest.*—In Tables 56 and 57 I have briefly summarized the statistics of insulation for oil and for glass. All reference is made to 215°, since these measurements are the more reliable. The table is not intended to convey more than a mere estimate of the conditions encountered.

TABLE 56.—*Breakdown of resistance in the case of the divers oils examined.*

	°	Sperm oil.	Gasoline.	Petroleum.	Thin mineral machine oil.	Very thick mineral machine oil.
Specific resistance at	215	3×10^6	1800×10^6	400×10^6	1000×10^6	1200×10^6
Relative resistance at	20	60	10	26	300	∞
Relative resistance at	100	7	2	9	30	30
Relative resistance at	215	1	1	1	1	1
Relative resistance at	310	..	1	·6	·5	·1

TABLE 57.—*Breakdown of resistance in the case of divers glass arrangements.*

[Specific resistance at 215°, 19×10^6.]

Glass in—	Sperm oil.	Gasoline.	Petroleum.	Thin mineral machine oil.	Thick mineral machine oil.
°					
100	500	....	1400	300	....
215	1	....	1	1	1
310	....	....	·2	·2	·05

DEDUCTIONS.

104. *Effect of pressure.*—It appears, from Table 48 et seq., that the pressure-coefficient does not decrease with the size of the pressure interval δp. The tendency is rather in favor of an increase; but this is obscure. Hence the results obtained are properties of either the oil or of the glass, and not incidental disturbances. Moreover, I am warranted in taking the means of the divers pressure coefficients found at any temperature as the probable value at that temperature.

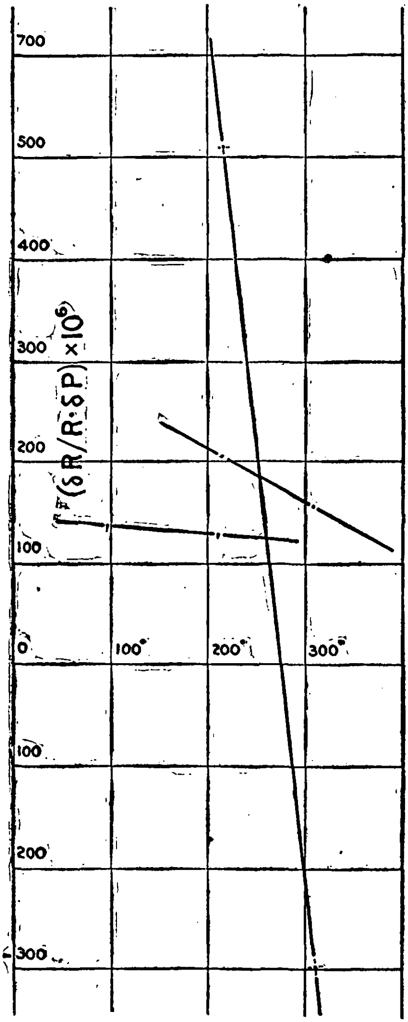

FIG. 22.—Pressure coefficient and temperture for thick mineral machine oil and for glass.

105. *Temporary and permanent effects.*—Remarks on the discrimination of temporary and permanent effects have been made in §§ 95, 97.

106. *Chart.*—In order to obtain a clear insight into the data of Tables 48 to 55, it is best to construct pressure coefficient as a function of temperature. This has been done in Figs. 18 to 22, above. It would be more in keeping with the present work to coordinate this coefficient with resistance; but the latter data are not sufficiently accurate.

107. *Pressure and chemical equilibrium.*—Turning attention first to the behavior of the solid insulator, it appears that the electrical resistance of glass increases in very marked degree with the pressure which is brought to bear on it. In my earlier paper[1], in which I subjected glass to tensile stress (presumably dilatational), I found that the resistance had pronouncedly decreased. I also found that the results at 360° were not as evident as at 100°. Hence the present and the earlier observations, though attacking the question from opposite points of view, are in accord. I am thus justified in announcing that *the chemical equilibrium of a solid changes with each change of strain* (§ 114).

108. *Effect of temperature.*—The tables further show that the pressure coefficient of resistance decreases with rise of temperature; or that the effect of pressure decreases algebraically as the number of free ions available for the transfer of charges become greater. In an earlier paper[2] I showed that the resistance of a liquid electrolyte like zinc sulphate in water, or of a liquid metal like mercury, is a decrease of specific resistance. Finally, the present results for insulating oils contain several examples in which a passage of the positive into the negative pressure coefficient is directly observed. I conclude that the curve for glass, if prolonged, will eventually intersect the axis of temperature somewhere in the region of low red heat, and that the further course will be negative. Hence for all substances, solid or liquid, there is a point or state of electrolytic dissociation at which the effect of pressure on resistance is nil, or at which the increased molecular stability obtained by pushing the molecules nearer together, and perhaps of binding the constituents of the individual molecule more firmly together, counterbalances the decrease of the path over which the ion travels in conveying charge. Taking all the results for glass, oils, the solution, and the metal into account, it appears that the complete functionality will be given by a curve which is asymptotic both to the vertical in the region of low temperatures and positive pressure coefficients, and to the horizontal in the region of relatively high temperatures and negative pressure coefficients. The nature of this curve I have not been able to work out (§ 106), nor will it be the same for all substances.

109. *Molecular effects of stress.*—Having thus found a consistent behaviour in metals and electrolytes in relation to strain, I am prepared to accept the proposition italicized in § 107 as true for solids[3] generally.

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[1] American Journal of Science (1889), vol. 37, p. 349.

[2] American Journal of Science (1890), vol. 40, p. 219.

[3] To my knowledge the only experiments on the effect of pressure on the resistance of solid metals are due to Chwolson (Carl's Repertorium, vol. 14, p. 26, 1878,) who shows that their pressure coefficient, like that of mercury, is negative.

For the case of metals Osmond[1] has partially anticipated me, stating that strain more or less completely converts cold metals from one definite molecular condition into another. I have been unable to find, however, that Osmond has any direct evidence to support this assertion, and I have already pointed out[2] some of the difficulties which Osmond must surmount before his view can gain general credence. If mechanical stress is to convert α-iron into β-iron, it is not to be overlooked that whereas the hardness called temper changes the electrical resistance of steel enormously (as much as 300 to 400 per cent), the electrical effect of mechanical strain is relatively negligible. Even though much of this discrepancy can be explained away, *direct* experiments on metals confirming Osmond's view will not be easily forthcoming. Two years ago I spent much time in endeavoring to throw light on the polymerization of metals, by studying the hydroelectrics of stretched and soft wires[3], by dissolving hard-drawn and annealed iron, by investigating the carburation changes of strained steel; but in no case have I found evidence of an indisputable bearing on the point at issue. Finally, regarding the mere statement[4] of inferences of the above kind, I believe I anticipated Osmond by interpreting viscosity in solids[4] with reference to Clausius's theory of electrolysis.

110. *Hysteresis.*—The proposition of § 107, taken in connection with my observation of the occurrence of volume lag[5], under isothermal conditions, suggests important inferences on the behavior of stress solids generally, and leads naturally to an explanation of hysteresis. If the pressure under which a liquid just solidifies, cæteris paribus, is in excess of the (positive or negative) external pressure at which it again liquefies (volume-lag[6]), and if the chemical equilibrium of the solid acted on changes with each change of strain, then, quite apart from consider-

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[1] Osmond: Ann. des Mines, July–August, 1888, p. 6; Mém. de l'artillerie de la marine (Paris, 1888), p. 4. Of course I make no reference against the ingenious experiments from which Osmond infers the spontaneous conversion of α-iron into β-iron at red heat.

[2] Nature, vol. 41, 1890, p. 370.

[3] American Chemical Journal, vol. 12 (1890), page 1.

[4] Am. Jour. Sci., vol. 33, 1887, p. 28.

[5] Am. Jour. Sci., vol. 38, 1889, p. 408.

[6] A good example of the volume-lag is given by an undercooled liquid like fused thymol (melting at 53°), for instance, which at, say, 30° solidifies under about 500 atm., and does not again liquefy on removing the external pressure. I have worked with para-toluidine, naphthalene, α-naphthol, paraffin, and caprinic, palmitic, and monochloracetic acids. My original belief in the general character of these static phenomena has recently been disturbed by new experiments, in which I found for the special case of paraffin that it would be possible to be misled by *local* solidifications of the column under pressure. The volume-lag is always marked when there is even a suggestion of undercooling. The action of pressure is then similar to the closing of a door and opening it again without lifting the latch. Observations made at intervals of 20 minutes each, with palmitic acid, showed that at 66° this substance solidifies between 300 and 400 atm., and then remains solid even between 200 and 300 atm. At 100°, α-naphthol solidifies at 500 to 600 atm., and when pressure is being removed it remains solid until about 150 atm. Undercooled caprinic acid at 20° solidifies under 150 atm., remaining solid. At 33° it solidifies at about 500 atm., and then fuses again at about 200 atm. Local solidifications here suggest the occurrence of isomers or other impurity. Sometimes, as in the case of naphthalene, the volume-lag is not thoroughly static, but becomes viscous in character, etc. I have yet to study the effect of temperature on the magnitude of the volume-lag, i. e., on the difference of pressures isothermally corresponding to solidification and to fusion. Very large pressure-intervals are essential for this purpose.

ations *directly* involving the second law of thermodynamics, quite apart from the energy dissipated in the cycle, the solid at identical stress points needs not to be in the same chemical condition while stress is being removed in which it was when stress was being applied; for there will be certain groups of particles, uniformly distributed throughout the solid, which during the "stress-on" phase pass from a first molecular condition to a second, and which, in virtue of the volume-lag, do not regain their original state at identical pressures of the "stress-off" phase. The march in the two cases is not a symmetrical one. This I take to be the inherent nature of the phenomena studied by Cohn[1], Warburg[2], and others, and to which Ewing[3], after much original research, has given the generic name hysteresis. In my note I pointed out the important bearing of the volume-lag on the molecular behavior of matter[4], though I have yet to specify my views in detail. The occurrence of hysteresis therefore implies a favorable molecular mechanism of the kind indicated, and one would not expect to find it at once in all substances.

Conformably with the above, the interpretation given by Mr. C. A. Carus-Wilson[5] of his important discovery (to which I alluded in a former paper) is much more than an analogy.

111. *Magnetic hysteresis.*—Warburg and Ewing have proved that hysteresis is not only associated with mechanical stress, but may be very clearly evoked by magnetic stress. Curiously enough, the evidence in favor of the views expressed in § 26 is here directly forthcoming. Remsen's[6] discovery of the chemical influence of the magnetic field, additionally substantiated as it now is by the ingenious experiments of Rowland and Bell[7], proves beyond a doubt that magnetic iron is more electro-negative than unmagnetic iron. Conformably with the above paragraphs, I therefore infer that this phenomenon is to be interpreted as directly evidencing a chemical difference between magnetic and unmagnetic iron, and as such I consider it an exceedingly important step towards an ion theory of magnetism[8]. Thus the occurrence

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[1] E. Cohn: Wied. Ann., vol. 6, 1878, p. 388.

[2] Warburg: Wied. Ann., vol. 13, 1881, p. 141.

[3] Ewing: Phil. Trans., vol. 2, 1885, p. 545.

[4] Am. Jour. Sci., vol. 38, 1889, p. 408.

[5] Carus-Wilson: Phil. Mag., vol. 29, 1890, p. 200.

[6] Remsen: Am. Chem. Jour., vol. 3, 1881, p. 157.

[7] Rowland and Bell: Phil. Mag. [5], vol. 26, 1888, p. 105.

[8] In Nature (vol. 41, 1890, p. 370) I pointed out that closed helical paths of molecular dimensions, each consisting of a right and a left hand screw-thread, with their ends joined, can be generated by the symmetrical interpenetration of two congruent Bravais nets. I inferred that electrical charges urged along and around the said closed helical paths by the action of the magnetic field could be made to replace the usual conception of molecular currents circulating in a molecule without resistance. From this point of view magnetic and electric fields merely differ in the rotational character of the former as compared with the nonrotational character of the latter. Whereas in an electrolyte the ion-dissociation takes place as the result of chemical relations and heat, it takes place in a metal under the mere influence of heat. The immediate action of both fields is directional; and by taking advantage of the positions of labile equilibrium of the ion, they act in a way analogous to Clerk-Maxwell's

of the chemical difference in question, and the explanation of magnetic hysteresis, as given in the present and preceding paragraphs, mutually sustain each other.

112. *Mechanism of viscosity.*—Whether viscosity and dissociation in solids are to be explained with reference to a single mechanism, or whether we are to conceive of two mechanisms (molecular and atomic frameworks), one, as it were, within the other, is at the present stage of research a mere question of special convenience. The remarkably low viscosity at the yield-points of metals, as well as the similarly low viscosity near the Gore-Barrett phenomena, are both in conformity with the sudden passage from a first molecular state to a second, through an instability.

It may be well to point out the bearing of the singular minimum[1] of the viscosity of hot iron on the interpretation given of Maxwell's theory,[2] more explicitly. When iron passes through Barrett's temperature of recalescence, its molecular condition is for an instant almost chaotic. This has now been abundantly proved.[3] The number of unstable configurations, or, more clearly, the number of configurations made unstable because they are built up of disintegrating molecules, is therefore at a maximum. It follows that the viscosity of the metal must pass through a minimum. Physically considered the case is entirely analogous to that of glass-hard steel suddenly exposed to 300°. If all the molecules passed from Osmond's β to his α state together, the iron or steel would necessarily be liquid. This extreme possibility is, however, at variance with the well-known principles of chemical kinetics. The ratio of stable to unstable configurations can not at any instant be zero. Hence the minimum viscosity in question, however relatively low, may yet be large in value as compared with the liquid state.

In a preceding bulletin (No. 73) I have shown that to explain the varied physical phenomena which accompany temper, it is sufficient to recognize some special instability in the tempered metal. This condition is given by the carbide configuration, and the physical explanations in question may be made without specifying its nature further. The essentially chemical nature of this phenomenon is, however, not to be ignored. Seeing that the amount of carbon contained in steel is not large, the electrical resistance of hard steel is at once an expression of its chem-

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demons ("Heat," chap. XXII, § 10), producing marked effects at the expenditure of a relatively small amount of work.

The advantage which I seek for in this tentative suggestion has direct reference to my own line of work. I can picture to myself the rôle played by the *foreign* ingredient chemically present in iron, in modifying the retentiveness and the magnetic stability of the metal. Thus I conceive the carbon atoms in hard steel to be so placed that after magnetization they block out definite closed helical paths in the metal, along which the transfer of charges must thereafter take place. Hence an increase of magnetic stability as contrasted with pure iron, where from any point four or more such paths may be open. Again, other substances (manganese, say) may be conceived to unite with the iron in such a way as to shut out the possibility of closed helical paths altogether. The fact that my permanent magnet is essentially a self-exhausting engine does not seem to be a serious objection.

[1] Roberts Austin: Nature, vol. 41, 1890, pp. 11, 34.

[2] Barus: Bulletin, U. S. Geol. Sur., No. 73, 1891.

[3] Cf. John Hopkinson: Phil. Trans., London, vol. 180, p. 443, 1889, where the literature may be found.

ical composition, structurally unknown though it be. Hence in the electrical diagram of the phenomena of temper, constructed by Dr. Strouhal and myself,[1] the time variations of resistance of hard steel at any given temperature may be interpreted as a case of Wilhelmy's[2] rate of chemical reaction, and expressed in accordance with his well-known exponential law. This indeed is the character of the observed curves. Hence also the full diagram of the phenomena of temper, considered both in their variation with time and with temperature, is available for the elucidation of moot points relative to the effect of temperature on rate of chemical reaction.

From all that has been said it is clear that the mechanisms of viscosity and of diffusion (electrolysis), though containing a similar thermal factor, can not be quite the same. Thus it has lately been shown by Reformatsky[3] that the speed of the same reaction in a jelly and in a water medium do not appreciably differ. On the other hand diffusion in solids is essentially a slow process. Studying the colored oxide coats on iron, Dr. Strouhal[4] and I pointed out that the outer surface of the film is oxidized as highly as possible in air; and that the inner surface of the film, continually in contact with iron, is reduced as far as possible. This distribution of the degree of oxidation along the normal to the layer, is equivalent to a force in virtue of which oxide is moved through the layer, from its external surface to its internal surface. The formation of an oxide coat is thus a case of diffusion. Conformably with this view, the film, during its formation, behaves like an electrolyte, as was discovered and substantiated by Franz, Gangain, and Jenkin, and more recently by Bidwell and by S. P. Thompson. We then adverted to the crucial difference between diffusion in solids and diffusion in liquids, inasmuch as in the former case (solids) diffusion demonstrably ceases after a certain small thickness is permeated. The limit thickness of the film is reached asymptotically through infinite time. It has a definite value for each temperature, increasing as temperature increases. In the light of other information since gained this explanation is substantiated. The formation of the oxide coat is a case of solid diffusion, and as such it bears the same relation to the diffusion of liquids that the viscosity of solids bears to the viscosity of liquids. The two phases (solid, liquid) of each phenomenon are to be correlated in ways essentially alike. The available stress, as compared with the available instability, determines the time character of the result.

To recapitulate: In the usual cases of viscosity there are presented to us cases of localized destructions of configurations, the integrant parts of which are stable molecules. In the case of chemical interaction between contiguous configuration (diffusion, electrolysis) consist-

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[1] Bulletin, U. S. Geol. Sur., No. 14, chapter II, 1885.

[2] Wilhelmy: Pogg. Ann., vol. 81, 1850, pp. 413, 499.

[3] Reformatsky: Zeitschr. f. phys. chem., vol. 7, 1891, p. 34.

[4] Bull. U. S. Geol. Sur., No. 27, 1886, p. 51.

ing either of an exchange of atoms or of molecules, there need be no viscous effect, provided the exchange is perfectly reciprocal. In the case of irreciprocal interaction, finally, by which molecules are left in the lurch and broken up, the configuration of molecules will also be modified, and hence a viscous effect appears. Examples of all these cases are frequent in the above text.

113. *Electrical effects of æolotropic stress.*—It follows from tables 48 to 55, that in an æolotropically strained transparent solid like glass, electric conduction is different in different directions, the difference depending on the intensity of strain. Suppose this be considered in connection with the doubly refracting property of such a solid, and again with Warburg and Tegetmeier's[1] researches on the electric conduction of quartz along its optic axis, with nonconduction at right angles to it. Then the inference is tenable, that the strain artificially sustained in one case is naturally sustained in the other. Tegetmeier's conducting sodic silicate, ingrained in the crystalline structure of quartz, and possessing larger molecular conductivity in quartz than in glass, may be looked to as responding to strain of the kind suggested.

UNAVOIDABLE ERRORS.

114. *Polarization.*—In the next six paragraphs it will be convenient to discuss some of the errors relating to both the measurements of resistance and electromotive force.

The effect of pressure on the polarization occurring in case of the above cell and of exceedingly weak currents is somewhat difficult to handle. Warburg[2] and others have shown that the reaction is essentially Na/glass/Hg changing to Na Na_2SiO_3glass/NaHg, or a mere transfer of sodium through the walls of the glass, by aid of sodium silicate as a conveyancer. I shall therefore have to rely on the data of Table 49, in which, if a marked effect of pressure on polarization had been present, it would have been detected. It will be remembered that I commenced with high initial pressures (p_0=50 to 200 atm.) to obviate incidental disturbances.

115. *Insulators.*—The effect of pressure on the oil in the piezometer was specially investigated in each case. Cf. Tables 50 to 55, § 122.

116. *Shifting isothermal planes.*—A source of error is introduced by the temporary shifting of the isothermal planes of the piezometer, during compression, in virtue of the compressibility of the oil contained in the tube. Adiabatic thermal changes during compression or removal of pressure would produce effects of a sign opposite to those of the tables.

To remove both of these it was often my habit to wait 3 to 5 minutes,

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[1] Warburg and Tegetmeier: Wied. Ann., vol. 35, 1888, p. 455; vol. 41, 1890, p. 18.

[2] Warburg: Wied. Ann., vol. 21, 1884, p. 622; vol. 35, 1888, p. 455.

supposing the original thermal state was then nearly enough regained. Longer waiting was not safe because of fluctuations of the astatic system of the galvanometer.

Special tests were made as follows: In Fig. 23 let P Q be the piezometer closed at Q, and receiving pressure in the direction of the arrow. Let A B be the position of the glass resistance tube. Finally, let the hollow cylindrical vapor bath surrounding the piezometer stretch respectively from *b* to *d*, or from *a* to *c*, or from *c* to *e*. Parts lying within the vapor bath have constant temperature, which falls off rapidly from both ends of the bath towards the ends of the piezometer. When pressure is applied the vertical isothermal planes of the compressible oil are all moved from P to Q. With the vapor bath in the position *b d*, pressure would thus cool the end A and heat the end B of the glass tube A B; but the cooling would exceed the heating. Hence an error of the sign of the data, Table I, etc. Now let the vapor bath be shifted to the position *a c* and the thermal state be steady. The B-half of the tube A B is now exposed to cold, and compression can only have the effect of heating these parts, seeing that the A-half is protected. Hence an error of a sign *opposite* to the data of Table 48, etc. Finally, when the bath has the position *c e*, the error first considered would be accentuated.

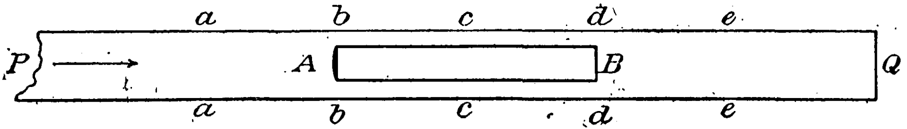

FIG. 23—Diagram.

I made experiments in accordance with this scheme at 310°, but found that this severe test did not change the character of the results of Table 48. Data are superfluous. Again, decreasing the length of the tube A B had no appreciable effect. Similar tests were made with reference to Table 49.

117. *Electromotive force.*—It is clear at the outset, since pressure increases both the resistance of glass and the electromotive force NaHg/glass/Hg, that changes of the latter will act in a way tending to wipe out the change of resistance. Let e, I, R denote the electromotive force, current, and resistance of the uncompressed circuit. Let I_p be the current corresponding to pressure p, and k_R and k_e be, respectively, the pressure-coefficients of resistance and electromotive force. Then

$$k_R = (I(1 + k_e p) - I_p)/p \, . \, I_p \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

Table 49 gives $k_e = 10/10^6$, say, whence the values of Table 58 result from Table 48, series III (cf. § 95). In the final column $k'_R = \delta R/R \, . \, \delta p$, the former coefficient.

TABLE 58.—*Allowance for increments of electromotive force.*

[$\theta=215°$.]

p	$10^3 p \,.\, k_e$	$I(1+pk_e)$	I_p	$10^6 \times k_R$	$10^6 \times k'_R$
523	5.2	21·18	19·47	168	157
995	9·9	21·28	18·11	175	164
1411	14·1	21·37	17·27	168	156
512	5·1	21·18	19·39	180	169
1016	10·2	21·28	18·07	172	163
1403	14·0	21·37	17·28	169	156

Thus the data underlying §§ 106, 107, 108 are accentuated. At 310° a permanent pressure-coefficient k_e could not be detected, and at 100° it is certainly very much in error (§ 118). Since therefore k_e is never fully vouched for, I have omitted it in the computation of k_R altogether.

118. *Short circuiting.*—In case of an uncompressed circuit shunted by unavoidable leaks, let R_1, R_2, R_3 be the resistances of the cell, the shunt, and the metallic circuit respectively. Similarly let i_1, i_2, i_3 be the three partial currents corresponding respectively to R_1, R_2, R_3. Let $\delta R_1/R_1$ be the effect of pressure on the resistance of the cell (resistance tube), and $\delta e/e$ be the simultaneous increment of electromotive force. Finally, in case of the compressed circuit, let accentuated symbols replace the symbols for the uncompressed cell. Then a somewhat tedious reduction leads to

$$R_1/R_1=\frac{i_3(1+\delta e/e)-i_3'}{i_3'}\,\frac{(1+R_2/R_1)\,(1+R_3/R_1)-1}{R_2/R_1-(n-1)\,R_3/R_1}, \quad . \quad . \quad . \quad . \quad (2)$$

$$\delta e/e=\frac{i_3'}{i_3}\,\frac{(\delta R_1/R_1)\,(R_2/R_1-(n-1)R_3/R_1)}{(1+R_2/R_1)\,(1+R_3/R_1)-1}-\frac{i_3-i_3'}{i_3}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\delta R_1/R_1=n\delta R_2/R_2$, and $\delta R_2/R_2$ is the pressure coefficient of the oil through which the leakage obviously takes place. Regarding $\delta R_1/R_1$ in (2), if the resistance, R_3, of the metallic circuit is relatively small, or if R_1 be reasonably small relative to the leak R_2, the considerations of § 111 at once apply. The case of $\delta e/e$, however, is serious. Supposing, again, that R_3/R_1 and R_1/R_2 are small, the last equation reverts to

$$-\delta e/e=(i_3-i_3'(1+\delta R_1/R_1))/i_3,$$

and thus the changes of resistance due to pressure are interpreted as changes of electromotive force. Zero or even electrometric methods will only measure the difference of potential of two points of the leak-shunted circuit. Hence the permanent pressure coefficients ($\delta e/e$) of Table 49 can not but be regarded with suspicion, and they are merely an essential justification of Table 48 et seq.

119. A final difficulty in case of short circuiting is not to be lost sight of. A leak usually includes an electrolyte between two different metals, and thus introduces an electromotive force in a way quite beyond computation.

120. *Electromotive force and pressure.*—The consideration of the data of Table 49 would now be in order; but for the reasons just stated I hold the work scarcely ripe for discussion, and will therefore withhold remarks until I can devise some more nearly faultless method of measurement.

121. *Graphic representation.*—In order to exhibit the full character of the individual observations of Tables 48 to 55, I shall discuss a series of data which I was first inclined to interpret as an electrical manifestation of volume "accommodation" (§ 101). In Fig. 24, A, B, C, the observed intensities of current in relative measure are given as ordinates. They are therefore inversely proportional to the resistance of the glass. The abscissæ are times, supposing that the times consumed in making each triplet of observations are equal and similar. The oscillations are due to the fact that pressure is raised from about 150 atmospheres to about 600 atmospheres, and then lowered to the first value again, thus giving the three points for each of the triplets numbered.

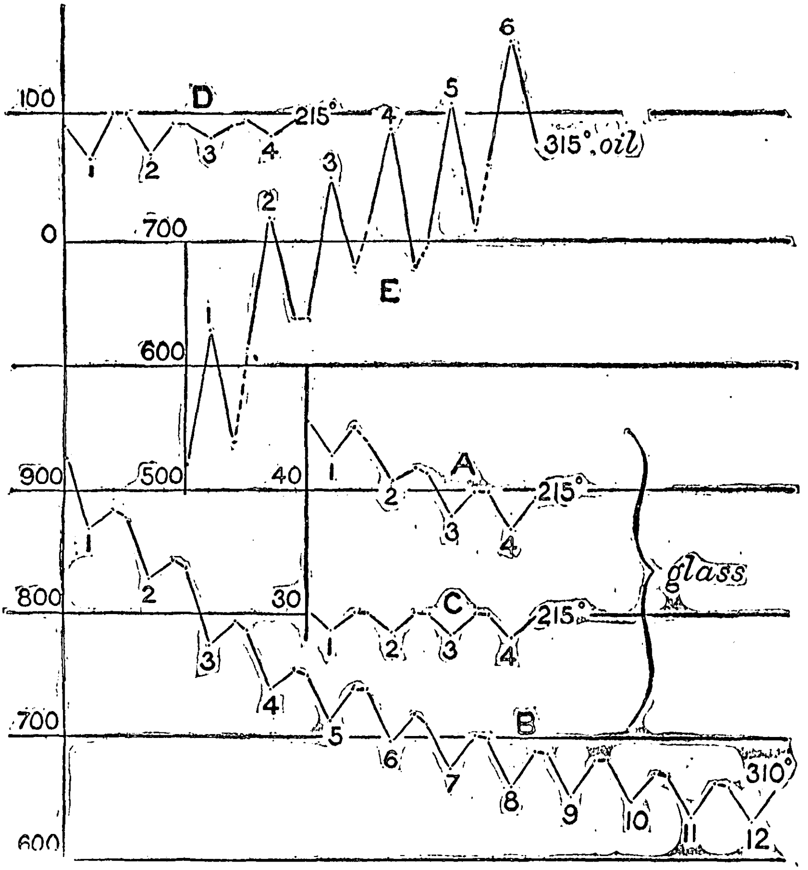

FIG. 24.—A, B, C: Charts showing the oscillation of the electric conductivity of glass with pressure at 215°, 310°, and again at 215° respectively. Experiments made consecutively. D, E: Charts showing the oscillation of the electric conductivity of very vicious hydrocarbon oil ("mineral machine oil") with pressure, at 215° and 315° respectively.

In Fig. 24, D, E, similar results are given for thick mineral machine oil. In the former, pressure was twice increased from about 160 to 980 atmospheres and back again; and then from about 160 to 540 atmospheres, thus obtaining amplitudes of different values. In E pressure oscillated between about 150 and 600 atmospheres.

A, B, C, which were obtained consecutively, show a gradual decrease of resistance to a limit, very obviously in A at 215°, quite as obviously in B at 310°, but not obviously, if at all, in C. Hence the inference is suggested that the continued exposure to strain alternations at 310° has wiped out all viscous instability possible at 215°. The volume elasticity of the glass, so far as its chemical manifestations are concerned, is now constant. The objections to this interpretation are twofold. In the first place the amplitudes of oscillation are constant throughout, cæt. par., and do not converge to a limit. Again, the results for oil show similar phenomena, not very obviously in D, but marked in E, where both the negative pressure coefficient and the resistance decrease act together to invert the figure.

122. *Electric instability of hydrocarbon oils.*—I have finally to refer to the results obtained with highly-insulating liquids. It appears from these that the effect on resistance of an additional number of molecules splitting up in consequence of the removal of a fixed amount of pressure, decreases rapidly with the total number splitting up, where the decrease is to be taken in an algebraic sense and to include a march through zero. In the case of sperm oil, gasoline, petroleum, thin and thick hydrocarbon machine oil, the observed pressure coefficients pass from positive towards or actually into negative values as temperature increases, and at a rate which for the same oil between 20° and 300° is nearly constant.

These rates ($\delta R/R . \delta p . \delta \theta$) are as follows:

TABLE 59.—*Rate of thermal variation of pressure coefficient.*

Sperm oil.	Gasoline.	Petroleum.	Thin mineral machine oil.	Thick mineral machine oil.
$-3/10^6$	$-9/10^6$	$-6/10^6$ $-10/10^6$	$-7/10^6$	$-6/10^6$

The figures therefore denote the change of the pressure coefficient per degree centigrade. In a general way it may be noted that this change is least in sperm oil, where ions are present in greatest number.

Similar remarks were made in my earlier paper[1], after an examination of mercury and solution of zinc sulphate. Both coefficients in this case were negative, and I was not prepared for the positive coefficients ($\delta R/R . \delta p$) so marked in the present paper. The data as a whole, therefore, show that it is not permissible to pass from one substance to another; doubtless because the number of molecules which must

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[1] Am. Jour. Sci., vol. 40, 1890 p. 222.

split up per unit of area to discharge the field varies largely from substance to substance. Inferences are to be drawn from one and the same solvent, either electrolytically dissociated by temperature, or modified by the solution of some given substance, or both.

123. The remarks of § 122 are substantiated by the incidental results of Table 53, where the number of ions is increased by dissolved dirt. It agrees with the negative pressure coefficient found for zinc sulphate (loc. cit.). Moreover, by keeping the thick machine oil at 310° for two or more hours, I found that its resistance continually decreased, while the pressure coefficient passed from indistinctly positive to pronounced negative values. Dissociation is here to be inferred.

I have only touched upon this question in passing; but if it can be proved that the occurrence of negative pressure coefficients is an index of solution, then metals may also be regarded as holding ions in solution. In general a sequence of changes of state or of molecule corresponding to gas-liquid, liquid-solid, may be regarded as crowded into the solid state, though the external manifestations are here no longer obvious at once.

124. *Conclusion.*—The present research has been excessively tedious and elusive. Moreover the final values for the pressure coefficient of glass (Tables 54, 55), although consistent, do not show the uniformity of values which I had hoped to reach. Nevertheless the results are marked, and unless there be some occult behavior of polarization, I do not believe that I have been led astray in my inferences. In so far as my results are correct, they contain the first direct and connected evidence of the change of chemical equilibrium with strain.

Regarding the behavior of liquid insulators like the hydrocarbon oils, the results found present many points of interest, and I have no doubt that a more systematic study of the subject than I have been able to make would throw much light on the details of the mechanism by which electricity is conveyed.

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