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UNITED STATES GEOLOGICAL SURVEY.

J. W. POWELL, DIRECTOR

REPORT OF WORK DONE

IN THE

DIVISION OF CHEMISTRY AND PHYSICS

MAINLY DURING THE

FISCAL YEAR 1884-'85

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MISCELLANEOUS ANALYSES.

PREFACE.

The present bulletin contains some of the more important results obtained in the chemical laboratory of the United States Geological Survey during the fiscal year 1884–'85. It also contains two physical papers representing work which was mainly done during previous fiscal years, but completed during the one for which this bulletin is issued. These papers are practically continuations of or supplements to Bulletin 14, and bear the names of C. Barus and V. Strouhal as joint authors. It will be remembered that Professor Strouhal was officially connected with the Survey under the administration of Mr. Clarence King, and the results here given were obtained by the authors partly before and partly since his resignation.

In addition to the work herein presented a considerable amount of material has accumulated in both our chemical and our physical laboratories, representing investigations which are still in progress, but which are not yet far enough advanced to warrant publication. For example, Dr. T. M. Chatard is engaged upon an investigation concerning the genesis of the North Carolina corundums; Dr. Gooch is examining a large series of geyser products from the Yellowstone Park; Dr. Barus has in hand some researches upon the measurement of high temperatures; Dr. William Hallock is studying the effect of pressure upon rock-forming material; and I am myself at work upon problems relating to the chemical constitution of the natural silicates. All of these investigations are being pushed as rapidly as possible, and the results will duly appear in future publications.

F. W. CLARKE,
Chief Chemist.

WORK DONE IN THE DIVISION OF CHEMISTRY AND PHYSICS IN 1884-'85.

TOPAZ FROM STONEHAM, MAINE.

By F. W. CLARKE.

In August, 1882, G. F. Kunz received from N. H. Perry, of South Paris, Me., some crystals which he immediately recognized as topaz. The locality from which they came was Harndon Hill, in the town of Stoneham, Oxford County, and subsequent explorations by Mr. Kunz and Mr. Perry brought to light much interesting material.[1] Later, the place became famous as a source of the very rare species herderite; and, in addition to this mineral and topaz, the locality has yielded specimens of albite (var. cleavelandite), apatite, autunite, biotite, beryl, columbite, damourite, fluorite, gahnite, garnet, muscovite, orthoclase, quartz, triplite, and zircon, together with other material of an obscure or doubtful character.

In the latter part of 1883, Mr. C. M. Bradbury[2] published an analysis of the Stoneham topaz, which, if correct, would show the mineral to be quite unlike any topaz hitherto known. His results were as follows, and make the proportion of fluorine half as high again as the generally accepted formula for topaz would require. The figures in parentheses are added to facilitate comparison with our own data:

Sp. Gr. 3.54.

Al	27.14	(Al_2O_3,51.26)
Si	14.64	(SiO_2, 21.37)
F	29.21	
O	28.56	
	99.55	

The peculiar interest attaching to these figures made a new analysis desirable; and accordingly the task was undertaken in this laboratory.

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[1] See paper by G. F. Kunz, in Proceedings of the American Association for the Advancement of Science, Vol. XXXII, 1883, p. 271.

[2] Chemical News, XLVIII, 109.

Meanwhile Mr. Perry had called our attention to some apparently altered topaz, the crystals of which, having the unchanged mineral at the center, were transformed upon the surface to a dark-purple soft substance, easily cut with a knife. Between the purple zone and the topaz was a greenish, intermediate layer, which shaded off imperceptibly into the original nucleus.

Intimately associated with the topaz, in all the specimens received by us, was a mineral identified by Dr. T. M. Chatard as damourite. This mineral occurs at the locality in two forms: first, as a broadly foliated mica, much like a pale-green muscovite, and sometimes very well crystallized; and, secondly, as a massive, subfibrous, dark-green variety, suggestive of steatite or serpentine. Both forms were analyzed by Dr. Chatard, and the analyses have already been published.[1] They are reproduced here for comparison in series with those of the topaz and its alterations. The latter were analyzed by Mr. Edward Whitfield, who examined the topaz itself, the greenish intermediate layer, and the outermost purple product. The topaz was white, massive, and somewhat milky, and the method of analysis was, as in the case of Bradbury's work, the old zinc-oxide process of Berzelius. The alkalies were estimated with the aid of the bismuth-oxide method of decomposition, as proposed by Hempel and modified in this laboratory by Chatard.[1] The results may be tabulated as follows:

	A—unaltered topaz.		*B*—greenish layer.		*C*—purple zone.		*D*—massive damourite.	*E*—foliated damourite.
Sp. Gr	3.51		3.42		2.82		......	......
Hardness	8.		7.		3.		......	......
SiO_2	31.92	......	35.15	......	44.52	......	45.19	45.34
Al_2O_3	57.38	......	53.18	......	46.19	......	33.32	33.96
F	16.99	17.21	12.88	......	0.40	0.38	......	......
H_2O	0.20	0.20	0.90	0.90	3.74	3.99	4.48	4.78
K_2O	0.15	0.12	1.52	......	2.30	......	11.06	10.73
Na_2O	1.33	1.18	1.28	......	2.82	......	1.57	1.49
FeO	......	......	......	......	......	......	4.25	3.96
MnO	......	......	......	......	0.21	......	0.58	0.51
CaO	......	......	1.32	1.42	0.30	0.48	trace.	0.22
MgO	......	......	0.17	0.14	0.14	......	0.36	0.10
	107.97		106.40		100.62		100.81	101.09
Deduct oxygen	7.16		5.42		.16			
	100.81		100.98		100.46			

If we now consider these analyses in their order, we find first that the topaz itself is ordinary topaz, having none of the anomalous character indicated by Mr. Bradbury's work. The small quantities of alkalies present may be attributed either to admixed impurity or to an incipient alteration such as is suggested by analyses B and C. The latter point clearly to a progressive change from topaz towards damourite, the fluorine and some alumina having been gradually eliminated

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[1] Bulletin No. 9, United States Geological Survey.

and replaced by other constituents. This change was probably brought about by the action of potash solutions, produced by the kaolinization of adjacent feldspathic material, the removal of fluorine and alumina having been followed by the taking up of potassium. One preliminary experiment bearing upon this mode of alteration has been tried. A weighed quantity of the topaz, in fine powder, from the sample which was analyzed by Mr. Whitfield, was digested on the water bath for seven days with a weak solution of potassium carbonate. Then, after filtering, the amount of fluorine in the filtrate was estimated, and found to be 0.38 per cent. of the weight of topaz taken. That is, fluorine can be slowly extracted from topaz by the suggested process, although further experiments are needed to make the case anything like complete.

In order to more completely prove the transformation of topaz into damourite, microscopic slides were made and examined by Mr. J. S. Diller,[1] who studied the specimen which showed the alterations most perfectly. In this specimen the purple zone had a thickness of about one centimeter and exhibited on its surface the crystalline faces of topaz. On other altered specimens even the topaz striæ were clearly visible. By means of the well-marked basal cleavage it was easy to prepare sections parallel and sections perpendicular to the vertical axis, and both sections extended from the outside of the purple border into the fresh topaz. The results of Mr. Diller's observations may be summarized as follows:

> In the topaz there are many liquid inclusions, from which the bubble readily disappears upon heating; and these are usually arranged in planes extending in nearly the same direction as and approximately parallel to the most common prismatic planes *I* and *i*-2̆. Almost at right angles to these are numerous fissures, which lie for the most part near the same prismatic planes. Some of these fissures are filled with a finely-foliated, micaceous mineral, whose physical and optical properties, as far as they can be observed, agree fully with those of the damourite which was subjected to analysis by Dr. Chatard. The foliæ of damourite occur in fissures only, and, although considerably interwoven, they are for the most part nearly parallel to the fissures in which they lie. In the section parallel to the vertical axis of the topaz the basal cleavage was plainly seen, and nearly parallel with the latter there were prominent cross fractures.
>
> The damourite extends far into the topaz along these basal fractures in the form of veins, and from the latter it sends off tongues into the prismatic fissures. These gradually increase in size, until the topaz entirely disappears, and the whole mass is made up of scales of damourite. The position of each scale bears no definite relation whatever to the crystallographic axes of the topaz; although the foliæ are generally parallel, they are often irregularly interwoven. The fact that between the mass of the topaz and the damourite there is an intermediate zone in which both are intermingled is exceedingly important. Furthermore, the damourite always occurs in fractures belonging to the topaz, indicating clearly that the fractures were formed before the damourite and determined its position. The basal fissures of the topaz, which depend upon its basal cleavage, once extended directly through the place now occupied by damourite, showing that the same space was once filled by topaz and that the former must be an alteration product of the latter.

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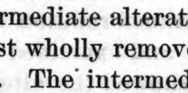
[1] See paper by Clarke and Diller; American Journal of Science, May, 1885.

It will at once be seen that the crystallographic and microscopic evidence is even more emphatic than the chemical analyses in pointing to the conclusion that the altered topaz is essentially damourite. And yet, if we compare the analysis of the purple material with the typical damourite examined by Chatard, we find that the transformation is chemically not quite perfect. More alumina must be lost and more potassium must be gained before the alteration can be considered completely damouritic; or, in other words, certain stages of the chemical process, although easily to be understood, are yet to be actually observed on specimens. The state of the case, as it stands in the actual specimens under consideration, is probably as follows: Analysis A represents practically unaltered topaz; B, a mixture of topaz, damourite, and an intermediate alteration product; C, a similar mixture, with the topaz almost wholly removed and the damourite overwhelmingly predominating. The intermediate product, which is perhaps microscopically identical with topaz itself, should be simply the latter species with its fluorine replaced either by oxygen, by hydroxyl, or by both; and its formation is probably a necessary antecedent to the production of the damourite. The loss of fluorine appears to have preceded the taking up of alkalies.

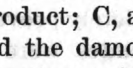
In order to make clear the relations between topaz and damourite, we may profitably consider a few structural formulæ. Reduced to its simplest empirical expression, the composition of typical topaz corresponds to the formula $Al_2\,F_2\,SiO_4$. This may be written structurally in seven different ways, three being as follows, and the others variations of these:

1.



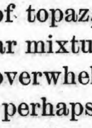
$$F_2{=}Si<\begin{matrix}O{-}Al{=}O\\O{-}Al{=}O\end{matrix}$$

2.



$$SiO_4\begin{matrix}\nearrow Al{-}F\\ \searrow Al{-}F\end{matrix}$$

3.

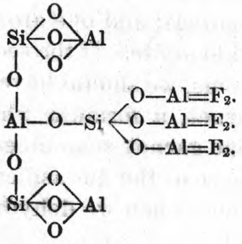


$$\begin{matrix} & \nearrow SiO_3\\ Al & \\ & >O\\ Al & \\ & \searrow F_2\end{matrix}$$

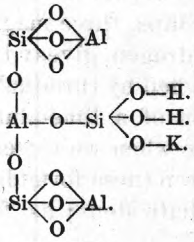
The first formula is rather improbable, the second represents an orthosilicate, the third falls under a metasilicate type. Which one is best supported by evidence?

A prime difficulty in the way of discussing the chemical structure of minerals arises from the fact that we have as yet no trustworthy means of ascertaining their true molecular weights. The formula of topaz, for example, may either be the simple expression given above or a multiple of that; and our only method of even approximately solving the problem is to study the reactions of topaz, or, in other words, its modes of alteration. Now, the simplest formula for pure damourite, and one which is commonly recognized, is $Al_3KH_2(SiO_4)_3$. That is, damourite is far more readily and probably figured as an orthosilicate than in any other way; and this fact tends to sustain the orthosilicate formula for topaz.

Inasmuch as the formula of damourite contains three SiO_4 groups, we may now triple the formula hitherto assigned to topaz, and write out in probable structural fashion the two formulæ side by side, thus—

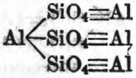


Topaz.



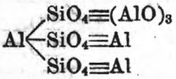
Damourite.

These results are suggestive even as they stand; but they become vastly more so if we consider with them a number of other mineral species, especially xenolite, fibrolite, paragonite, and eucryptite. Xenolite, it will be remembered, is optically almost identical with fibrolite; fibrolite is unquestionably related to topaz; paragonite is the sodium analogue of damourite, and eucryptite is notable for its easy alterability into mica. Tripling the formulæ commonly assigned to fibrolite and eucryptite and using a somewhat more condensed graphical notation, the series may be represented as follows:



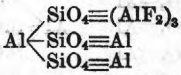
$\mathrm{Al}\left<\begin{array}{l}\mathrm{SiO_4}\equiv\mathrm{Al}\\ \mathrm{SiO_4}\equiv\mathrm{Al}\\ \mathrm{SiO_4}\equiv\mathrm{Al}\end{array}\right.$

Xenolite.



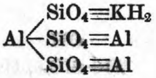
$\mathrm{Al}\left<\begin{array}{l}\mathrm{SiO_4}\equiv(\mathrm{AlO})_3\\ \mathrm{SiO_4}\equiv\mathrm{Al}\\ \mathrm{SiO_4}\equiv\mathrm{Al}\end{array}\right.$

Fibrolite.



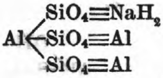
$\mathrm{Al}\left<\begin{array}{l}\mathrm{SiO_4}\equiv(\mathrm{AlF_2})_3\\ \mathrm{SiO_4}\equiv\mathrm{Al}\\ \mathrm{SiO_4}\equiv\mathrm{Al}\end{array}\right.$

Topaz.



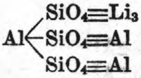
$\mathrm{Al}\left<\begin{array}{l}\mathrm{SiO_4}\equiv\mathrm{KH_2}\\ \mathrm{SiO_4}\equiv\mathrm{Al}\\ \mathrm{SiO_4}\equiv\mathrm{Al}\end{array}\right.$

Damourite.



$\mathrm{Al}\left<\begin{array}{l}\mathrm{SiO_4}\equiv\mathrm{NaH_2}\\ \mathrm{SiO_4}\equiv\mathrm{Al}\\ \mathrm{SiO_4}\equiv\mathrm{Al}\end{array}\right.$

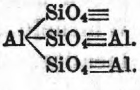
Paragonite.



$\mathrm{Al}\left<\begin{array}{l}\mathrm{SiO_4}\equiv\mathrm{Li_3}\\ \mathrm{SiO_4}\equiv\mathrm{Al}\\ \mathrm{SiO_4}\equiv\mathrm{Al}\end{array}\right.$

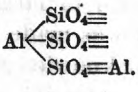
Eucryptite.

Xenolite, it will be observed, is the normal orthosilicate of aluminum; and from its formula, by simple substitution, the other formulæ are developed. This fact at once suggests the generalization that all or nearly all orthosilicates containing aluminum may be structurally regarded as substitution derivatives of the normal salt, a view which appears to be justified by many facts, and which I am endeavoring to work out in detail. A full discussion of the subject is reserved for the future, but for present purposes a few illustrations may be given. For instance, the orthosilicate micas, notably the typical muscovites, biotites, and phlogopites, may all be represented as derivatives of the following unsaturated nuclei:



$\mathrm{Al}\left<\begin{array}{l}\mathrm{SiO_4}\equiv\\ \mathrm{SiO_4}\equiv\mathrm{Al}.\\ \mathrm{SiO_4}\equiv\mathrm{Al}.\end{array}\right.$

Muscovite nucleus.



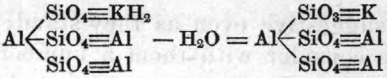
$\mathrm{Al}\left<\begin{array}{l}\mathrm{SiO_4}\equiv\\ \mathrm{SiO_4}\equiv\\ \mathrm{SiO_4}\equiv\mathrm{Al}.\end{array}\right.$

Biotite nucleus.

$\begin{array}{l}\mathrm{Al}\left<\begin{array}{l}\mathrm{SiO_4}\equiv\\ \mathrm{SiO_4}\equiv\\ \mathrm{SiO_3}\end{array}\right.\\ \mathrm{Al}\left<\begin{array}{l}\mathrm{SiO_4}\equiv\\ \mathrm{SiO_4}\equiv\end{array}\right.\end{array}$

Phlogopite nucleus.

The first of these three we find in damourite; the second, saturated with two atoms of ferrous iron, one atom of hydrogen, and one atom of potassium, fairly represents Lewis's siderophyllite; the third, satisfied by two MgF groups, three magnesiu m atoms, and one atom each of potassium and hydrogen, gives a typical phlogopite. If the second nucleus were to be satisfied by three calcium atoms, we should have represented the composition of a lime-alumina garnet, a formula which becomes very suggestive when we remember that garnet sometimes alters into biotite. Between these formulæ and those of the metasilicate micas are many intermediate steps; as, for example, when we dehydrate damourite, thus —

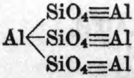


$$\mathrm{Al}\left<\begin{array}{l}\mathrm{SiO_4{\equiv}KH_2}\\ \mathrm{SiO_4{\equiv}Al}\\ \mathrm{SiO_4{\equiv}Al}\end{array}\right. - \mathrm{H_2O} = \mathrm{Al}\left<\begin{array}{l}\mathrm{SiO_3{\equiv}K}\\ \mathrm{SiO_4{\equiv}Al}\\ \mathrm{SiO_4{\equiv}Al}\end{array}\right.$$

As the lepidolite group of micas is now under investigation in this laboratory, the further discussion of mica formulæ is postponed.

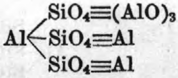
Two other series of formulæ bearing upon this system of representation are as follows:

1.



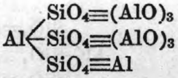
$$\mathrm{Al}\left<\begin{array}{l}\mathrm{SiO_4{\equiv}Al}\\ \mathrm{SiO_4{\equiv}Al}\\ \mathrm{SiO_4{\equiv}Al}\end{array}\right.$$

Xenolite.



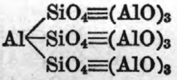
$$\mathrm{Al}\left<\begin{array}{l}\mathrm{SiO_4{\equiv}(AlO)_3}\\ \mathrm{SiO_4{\equiv}Al}\\ \mathrm{SiO_4{\equiv}Al}\end{array}\right.$$

Fibrolite.



$$\mathrm{Al}\left<\begin{array}{l}\mathrm{SiO_4{\equiv}(AlO)_3}\\ \mathrm{SiO_4{\equiv}(AlO)_3}\\ \mathrm{SiO_4{\equiv}Al}\end{array}\right.$$

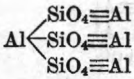
Dumortierite.



$$\mathrm{Al}\left<\begin{array}{l}\mathrm{SiO_4{\equiv}(AlO)_3}\\ \mathrm{SiO_4{\equiv}(AlO)_3}\\ \mathrm{SiO_4{\equiv}(AlO)_3}\end{array}\right.$$

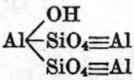
Unknown.

2.



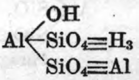
$$\mathrm{Al}\left<\begin{array}{l}\mathrm{SiO_4{\equiv}Al}\\ \mathrm{SiO_4{\equiv}Al}\\ \mathrm{SiO_4{\equiv}Al}\end{array}\right.$$

Xenolite.



$$\mathrm{Al}\left<\begin{array}{l}\mathrm{OH}\\ \mathrm{SiO_4{\equiv}Al}\\ \mathrm{SiO_4{\equiv}Al}\end{array}\right.$$

Westanite.



$$\mathrm{Al}\left<\begin{array}{l}\mathrm{OH}\\ \mathrm{SiO_4{\equiv}H_3}\\ \mathrm{SiO_4{\equiv}Al}\end{array}\right.$$

Kaolin.

$$\mathrm{Al}\left<\begin{array}{l}\mathrm{OH}\\ \mathrm{SiO_4{\equiv}H_3}\\ \mathrm{SiO_4{\equiv}H_3}\end{array}\right.$$

Montmorillonite.

The suggestiveness of such formulæ can hardly be questioned, and a close examination of them will show that they also fulfill the main purpose of structural formulæ; namely, that they indicate probable lines for fruitful synthetic research.

One more question may be included within the scope of the present paper. What has become of the fluorine withdrawn from the topaz during the process of alteration? The answer is probably not far to seek. Leached out from the topaz in the form of alkaline fluorides, it entered into new modes of union, and these are represented at the locality by the species fluorite, herderite, and apatite. The last-named mineral occurs in small crystals, and also in large dark-green masses. As an analysis of the massive apatite was made by Mr. Whitfield, I subjoin it, as a further contribution to our knowledge of the locality. The specific gravity was 3.27 and the mineral became colorless on heating.

CaO	47.60
MgO	6.08
FeO	1.44
P_2O_5	40.36
Cl	.29
F	6.84
H_2O	.11
	102.72
Deduct oxygen	2.94
	99.78

The high proportion of fluorine found in this analysis was undoubtedly due to intermixed fluorite. The large amount of magnesia, moreover, suggests the desirability of a careful search at the locality for wagnerite.

ON THE SEPARATION OF TITANIUM AND ALUMINUM, WITH A NOTE ON THE SEPARATION OF TITANIUM AND IRON.

By F. A. GOOCH.

In attempting to separate titanium and aluminum it is usual to resort to that method which depends upon the action of the slightly acid solution of the sulphates when submitted to prolonged boiling. The faultiness of this method, however, becomes apparent when solutions of aluminum and titanium are compared as to behavior under the conditions. To secure the complete precipitation of titanium the excess of sulphuric acid must be kept small, while to prevent the deposition of alumina the acid must be more than enough to dissolve the same amount freshly precipitated as hydrate, in the cold. Thus, upon boiling solutions containing the equivalent of .06 grm. of titanic oxide, 2.5 grm. of free sulphuric acid, beside alkaline sulphates, in 800 $cm.^3$ of water, it was found that at the end of an hour .003 grm. of titanic oxide in one case and .006 grm. in another experiment had escaped precipitation; but that, when the solution of titanium had first been precipitated by ammonia and then made just acid by sulphuric acid, every trace of dissolved titanium was thrown out on boiling. The experiment, on the other hand, of boiling a gramme of alum—roughly speaking 0.1 grm. of alumina—in 800 $cm.^3$ of water shows almost immediately the deposition of some alumina, and the same thing happens when the alumina is first precipitated by ammonia and then dissolved by just enough sulphuric acid to effect the solution. The difficulty of so adjusting the acidity of the solution that no alumina shall be deposited and no titanium held up is obvious. Test paper is of no aid in the case, since the reaction of alum itself and aluminic sulphate is acid. Under the circumstances it is hardly surprising that Knop[1] should revert from the troublesome, and only under remote conditions more exact, method of separation by boiling to the convenient but indubitably inaccurate process of parting by the use of sodic hydrate. Knop employs both the dry and the wet method—the fusion of the oxides in sodic hydrate and the treatment of the salts in solution with sodic hydrate in excess; but both had long before been generally discarded, and the single ex-

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[1] Jahrb. f. Min. 1876, p. 756; Zeit. f. Kryst. u. Min., I. 58.

periment of acidulating the alkaline filtrate from a precipitate obtained by the treatment of a pure titanium salt according to either mode, and then making alkaline with ammonia, is enough to prove their worthlessness.

In an endeavor to secure a better means of separating titanium from aluminum I have followed two lines of experimentation—the one based upon the observation that, under properly-controlled conditions, titanium is completely precipitated and alumina held in solution when an alkaline orthophosphate, strongly acidified with formic acid, is added to the solution of salts of these elements; the other, upon the solubility of alumina and the insolubility of titanic hydrate in sufficiently strong boiling solutions of acetic acid. Two preparations of titanium were used as test material in the course of the work — the solution of the fusion in sodic bisulphate of the hydrate precipitated by ammonia from the fluoride of titanium and potassium itself made from rutile and carefully purified by recrystallization; and the solution obtained by treating the carefully-prepared double fluoride with sulphuric acid, evaporating to dryness, redissolving in sulphuric acid, and diluting with water. The second mode of preparation is the better, because the amount of alkaline sulphate present in the test solution is much smaller. At first, the strength of the solution was fixed by precipitating weighed amounts by ammonia, carefully washing, igniting, and weighing the precipitate; but in the course of the work it became plain that the precipitation by means of ammonic acetate, or by ammonia with the subsequent addition of acetic acid in distinct excess, yielded more precise results. On this account, therefore, the determinations of the standard of the solutions employed in the later work were made by the acetic acid process, and the determinations by ammonia were corrected to correspond. In some of the experiments bearing upon this point, the results of which are given in the figures below, precipitations by ammonia were made in the cold and the liquid then heated to boiling; in those in which acetic acid was used just in excess, this reagent succeeded the ammonia at once, and the boiling followed; when precipitation was effected in presence of large amounts of acetic or formic acid, the acid was added in the amount intended, sodic acetate in quantity more than that necessary to decompose the sulphates present was introduced, and the clear solution heated to boiling, and kept boiling for a minute or two. The acetic acid employed was the C. P. article of commerce, and contained thirty-five per cent. of absolute acid. The amounts of it used — 20%, 30%, 40%, 50% by volume — correspond to 7%, 10.5%, 14%, 17.5% of absolute acid. The formic acid contained twenty-seven per cent. of pure acid, and when it is said that there was in solution 5.4% of it, the absolute acid is meant; but it was the weaker acid, to the amount of 20% of the entire volume, which was actually used. The experiments were made in sets, and so appear in the record, in consequence of changes (due to slight depositions from time to time) in the strength of the test solution, which necessitated redeterminations of standard.

	Weight of solution.	TiO₂ found.	TiO₂ in 50 grm.	Mode of precipitation.
(1)	52.7370 grm.	0.3177 grm.	0.3012 grm.	By ammonia.
(2)	52.7610 “	0.3180 “	0.3012 “	
(3)	52.7620 “	0.3076 “	0.2912 “	By ammonia and excess of acetic acid.
(4)	41.8010 “	0.2436 “	0.2914 “	
(5)	52.9420 “	0.3381 “	0.3193 “	By ammonia.
(6)	53.0200 “	0.3384 “	0.3191 “	
(7)	10.6300 “	0.0667 “	0.3137 “	By acetic acid 7% by volume.
(8)	10.6960 “	0.0671 “	0.3137 “	
(9)	21.1030 “	0.1285 “	0.3044 “	By ammonia.
(10)	21.1480 “	0.1290 “	0.3049 “	
(11)	21.0810 “	0.1248 “	0.2960 “	By acetic acid 14% by volume.
(12)	21.1670 “	0.1259 “	0.2974 “	
(13)	21.0620 “	0.1270 “	0.3015 “	By ammonia.
(14)	21.2310 “	0.1279 “	0.3012 “	
(15)	10.4370 “	0.0617 “	0.2956 “	By acetic acid 10.5% by volume.
(16)	10.6590 “	0.0629 “	0.2950 “	
(17)	10.4870 “	0.0618 “	0.2946 “	By acetic acid 14% by volume.
(18)	10.8820 “	0.0637 “	0.2940 “	
(19)	10.4700 “	0.0615 “	0.2938 “	By formic acid 5.4% by volume.
(20)	10.7410 “	0.0627 “	0.2919 “	
(21)	52.3960 “	0.3396 “	0.3230 “	By ammonia.
(22)	52.4140 “	0.3378 “	0.3222 “	
(23)	52.6350 “	0.3340 “	0.3262 “	
(24)	52.5600 “	0.3372 “	0.3208 “	By acetic acid in distinct excess.
(25)	52.4830 “	0.3366 I “ 0.3363 II “	0.3207 “ 0.3204 “	
(26)	52.3700 “	0.3348 “	0.3196 “	By acetic acid 17.5% by volume.
(27)	52.6420 “	0.3374 “	0.3205 “	

It will be noticed in the examination of these figures that parallel determinations usually agree very closely. The amounts of titanic oxide indicated by those experiments in which the precipitation was made by ammonia are much in excess of those in which acetic acid was added subsequently. Thus the difference between (1), (2) and (3), (4) amounts to more than three per cent. of the total amount of the former; that between (5), (6) and (7), (8), to a little less than two per cent.; that between (9), (10) and (11), (12), to about two and a half per cent.; and a correction of more than two per cent. must be applied to (13), (14) to bring them to correspondence with (15), (16), (17), (18). The difference between (21), (22), (23) and (24), (25), (26), (27) is about one per cent., and the smallness of this figure in comparison with the differences previously noted is apparently explicable by the fact that the solution of titanium employed in the last determinations was prepared by the second of the methods mentioned above and carries a smaller amount of alkaline sulphate. The ten dency of titanic hydrate to include the sulphates of the alkalies is not strange in view of the well known conduct of aluminic hydrate under similar circumstances, but the amount thus held is rather surprising. The experiments in which different proportions of free acid were introduced go to show, very strikingly, that, if acetic acid exerts any solvent action whatever upon the precipitate thrown down by boiling the acetate, that action is very slight. Thus, between the mean of (24), (25) and that of (26), (27,)—the one set precipitated by ammonia and treated before boiling with just a distinct excess of acetic acid, the other pair thrown out of a large volume, 700 cm.^{3}, one-half of which was acid of 35% strength, by boiling—we find a difference of but 0.0007 grm., and between the mean of (15), (16) and that of (17), (18), the difference (magnified five times by reference to 50 grm. portions) is 0.0010 grm.

In (25), too, we have an experiment in which the weighed precipitate was fused in sodic carbonate, dissolved, and again precipitated as before and weighed, the two weights differing by 0.0003 grm. Moreover, the filtrates from the precipitates thrown out in presence of an excess of acetic acid, when neutralized with ammonia, failed invariably to show the smallest precipitate, and in direct experiments upon the sensitiveness of the reaction it was found that on the addition of 0.0005 grm. of titanic oxide in solution to 100 cm.^{3} of 35% acetic acid carrying a little sodic acetate a distinct precipitate appeared almost immediately on boiling. It is plain, therefore, that so far as concerns the purpose in hand the insolubility of the titanium precipitate in acetic acid may be taken as absolute. The small apparent losses to be observed in some of the determinations in which a large excess of acetic or formic acid was employed are probably explicable by the tendency of the precipitate to change its consistency as the amount of free acid increases, and, in very acid solutions, to show an inclination to adhere in small amounts, but quite persistently, to the vessel in which precipitation takes place. The adherent precipitate may be dislodged with ease by putting a little hydrochloric acid into the beaker to which the precipitate adheres, covering and heating gently so that the acid volatilized may condense upon the walls of the beaker and again run down. By then rubbing the walls of the beaker a little and adding ammonia in excess, the trace of residual titanium is completely recovered. This method of recovery was applied in (26), (27).

In preliminary experiments upon the first of the methods which seemed to promise a separation of titanium and aluminum, it was found that the precipitation of titanium by an alkaline orthophosphate is complete in the presence of a large amount of acetic or formic acid, and that, in the cold, and under conditions otherwise properly controlled, aluminic phosphate fails to appear. To hold up the alumina by means of acetic acid requires some care in the adjustment of the acid and phosphate, and to redissolve the precipitate once formed is a matter of considerable difficulty. Thus, to clear the solution of a precipitate produced by 1.5 grm. of the phosphate of soda and ammonia upon 0.1 grm. of alumina, it was necessary to dilute the liquid to a volume of 250 cm.^{3} and add acetic acid until there was in the solution at least five per cent. of absolute acid; and the addition of 1.5 grm. more of the precipitant again precipitated aluminic phosphate. Formic acid, however, is more active, and the balance between it and the precipitant not so delicate. When the proportion of three parts by weight of absolute formic acid to two parts of microcosmic salt is kept, the aluminic phosphate does not fall; and if, because of a deficiency of acid, precipitation does take place, the liquid immediately clears as soon as the proportion of acid and precipitant is restored. Formic acid, therefore, was used in the experiments about to be described. The test solution of titanium was that employed in the previous experiments (1) to (20), but, inasmuch as the error of the process had not yet been remarked, the standards were determined by precipitating by ammonia, and are therefore to be corrected. The application of a correction of two and one-half per cent. to the apparent weights of titanic oxide found by the ammonia process—the mean correction for (1), (2), (5), (6), (9), (10), (13), (14)—cannot lead far away from the truth, since the difference between the maximum and minimum corrections observed amounts for the quantity of material employed in these experiments to but 0.0002 grm. Determinations of standard, original and corrected, are given in (28), (29), (30), and (31).

	Weight of solution.	TiO_2 found.	Corrected TiO_2 in 50 grm.	Corrected TiO_2 in 50 cm.^{3}
(28)	52.7660 grm.	0.3867 grm.	0.3572 grm.	0.3771 grm.
(29)	52.8410 "	0.3869 "	0.3569 "	
(30)	52.5380 "	0.3810 "	0.3627 "	
(31)	52.6920 "	0.3822 "	0.3627 "	

A portion of the solution, the standard of which is set by (28) and (29), was diluted to ten times its volume, and 50 cm.^{3} of the diluted solution were used in each of the experiments immediately following. These were made to determine whether the precipitate was definite in composition and might be weighed as such. Precipitation was effected by a solution of microcosmic salt acidified with formic acid. The precipitates of (32) and (33) were collected on paper, that of (34) on asbestus, and all were ignited and weighed directly.

	Amount taken.	TiO_2 and P_2O_5 found.	TiO_2 by standard.	P_2O_5 by difference.
(32)	50 cm.^{3}	0.0731 grm.	0.0377 grm.	0.0354 grm.
(33)	"	0.0640 "	0.0377 "	0.0263 "
(34)	"	0.0753 "	0.0377 "	0.0376 "

The phosphate obtained by Merz[1] by precipitating in presence of hydrochloric acid containing two molecules of TiO_2 to one of P_2O_5 requires 0.0326 grm. of P_2O_5 to 0.0377 grm. of TiO_2. It will be noticed that in two determinations the P_2O_5 is in considerable excess of the amount demanded by this proportion, and in one, in deficiency. The idea of

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[1] Jour. prakt. Chem., XCIX, 157.

weighing the phosphoric anhydride and titanic oxide together was therefore abandoned.

In experiments (35), (36), (37), the titanium was present alone; in (38), (39), 2 grms. of alum were added to the solution before precipitating by means of the mixture of microcosmic salt and formic acid, 5 grm. of the former being employed to 8 grm. of the latter. The precipitates of all, excepting (35), were carefully washed, ignited, fused with sodic carbonate, and the product of fusion was dissolved in water, the insoluble titanate separated from the soluble phosphate by filtration and washing, ignited, again fused with a little sodic carbonate, the result of fusion dissolved in strong sulphuric acid, diluted with water, and precipitated by ammonia with the subsequent addition of acetic acid, and boiling. Experiment (35) was conducted in like manner, excepting that the sodic titanate was dissolved off the filter by means of a mixture of hydrochloric and oxalic acids, the latter destroyed by potassic permanganate (since there is danger that in presence of ammonic oxalate the titanium may not be completely precipitated by ammonia), ammonia added in excess, then acetic acid to strongly acid reaction, and the liquid boiled. This mode of treating the acid titanate is not desirable, since the titanic hydrate, if precipitated but once subsequently, retains a trace of manganese. To fuse the titanate with sodic carbonate, and then treat the melt with strong sulphuric acid, is probably the best way of getting the titanium into solution again. The test solution of (28) and (29) was employed in experiment (35) and that of (30) and (31) in the rest.

From experiments (36) and (37), together with (35), which, as has been remarked, would naturally give figures slightly too high, it appears that the method indicates with accuracy the amount of titanium present. Experiments (38) and (39) indicate that the separation from alumina is not unreasonably inexact.

	Weight of solution.	TiO_2 found.	TiO_2 by standard.	Error.	
(35)	5.2220 grm.	0.0383 grm.	0.0373 grm.	0.0010 grm.	+
(36)	5.2300 "	0.0371 "	0.0370 "	0.0001 "	+
(37)	5.3840 "	0.0380 "	0.0381 "	0.0001 "	—
(38)	5.2920 "	0.0367 "	0.0374 "	0.0007 "	—
(39)	5.2540 "	0.0383 "	0.0372 "	0.0011 "	+

The tediousness of filtration, which is a consequence of the nature of the phosphate precipitate, is the great objection to the method, and on account of it the testing was pushed no further, attention being turned instead to the second line of experimentation.

The incompleteness of the precipitation of alumina by the basic acetate process in presence of a large excess of acetic acid, suggested the attempt to hold up alumina entirely by means of a sufficient excess of acetic acid while precipitating titanium. Experiments to determine the amount of acetic acid necessary to prevent the precipitation of alumina from a boiling solution of the acetate, indicate that amounts of absolute acid in excess of five per cent. by volume of the solution are adequate to the purpose, and that the addition of sodic acetate in reasonable amounts does not sensibly affect conditions. It appears, further, that the addition of a very small quantity of titanium in solution to the clear boiling solution of alumina in acetic acid occasions at once a perceptible precipitation. Thus, 0.0005 grm. of titanic oxide in solution produced a distinct and appreciable opalescence in 500 cm.^{3} of liquid containing 10 grm. of alum, 15 grm. of sodic acetate (about twice the amount necessary to convert the sulphate of alumina to the acetate), and seven per cent. by volume of absolute acetic acid.

In respect to holding up alumina, formic acid acts like acetic acid, but more potently.

In the following experiments to test the method quantitatively two solutions of titanium were employed: in (40) and (41), the solution the value of which was fixed by (15) to (18); in (42) to (46), the solution whose standard was set by (24) to (27). To the cold solution of titanium containing a little free sulphuric acid, together with some alkaline sulphate, were added 5 grm. of alum (approximately 0.5 grm. of alumina), 20 grm. of sodic acetate (which was always more than enough to effect the entire conversion of the aluminic and titanic sulphates to acetates), acetic acid to such amount that in experiments (42), (43), (44) there should be in the solution seven per cent. by volume of absolute acid and in the remaining experiments ten and one-half per cent. by volume, and water to make the entire volume 250 cm.^{3} in (40) and (41) and 400 cm.^{3} in the rest. The clear solutions obtained in this manner were raised quickly to boiling, kept at that point for a minute, and removed from over the burner so that the precipitate might settle, as it does almost immediately. The supernatant liquid was decanted upon a filter sufficiently porous to permit very rapid filtration,[1] and the precipitate added immediately thereafter and washed with 7% acetic acid, followed finally by hot water. The washed precipitate was dried, ignited, and weighed. The precipitate once upon the filter and drained becomes more compact and easily washed, and strong ignition of fifteen or twenty minutes over a good Bunsen burner, after the paper is thoroughly ashed, reduces it to a weight which neither the blast-lamp nor ignition in an atmosphere of ammonic carbonate changes.

	Weight of solution.	TiO_2 found.	TiO_2 by standard.	Error.	
(40)	10.4910 grm.	0.0645 grm.	0.0618 grm.	0.0027 grm.	+
(41)	10.5970 "	0.0656 "	0.0624 "	0.0032 "	+
(42)	20.9520 "	0.1450 "	0.1343 "	0.0107 "	+
(43)	21.1750 "	0.1439 "	0.1357 "	0.0082 "	+
(44)	21.0250 "	0.1431 "	0.1347 "	0.0084 "	+
(45)	20.8740 "	0.1393 "	0.1338 "	0.0055 "	+
(46)	21.0570 "	0.1402 "	0.1349 "	0.0053 "	+

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[1] The paper No. 589 of Schleicher and Schüll is excellent for the purpose.

It is quite obvious that a single precipitation by the method used does not yield titanic oxide free from alumina. The weighed precipitate of each experiment was therefore fused with a small quantity of sodic carbonate, and the product of fusion treated in the crucible with strong sulphuric acid, which gradually with the aid of gentle heat dissolved everything completely. This solution after cooling was poured directly into 100 cm.^{3} of cold water, and, the liquid remaining clear, ammonia was added just to alkalinity, and then dilute sulphuric acid corresponding to 2.5 grm. of pure acid. The precipitate thrown down by ammonia was gradually, but after a few minutes, entirely redissolved, acetic acid was added until it amounted in terms of absolute acid to ten and one-half per cent. of the entire volume, 20 grm. of sodic acetate were introduced, the solution was boiled, and the precipitate treated as previously described. The results of this second treatment are given below.

	Weight of solution.	TiO_2 found (II).	TiO_2 by standard.	Error.	
(40)	10.4910 grm.	0.0624 grm.	0.0618 grm.	0.0006 grm.	+
(41)	10.5970 "	0.0623 "	0.0624 "	0.0001 "	—
(42)	20.9520 "	0.1373 "	0.1343 "	0.0030 "	+
(43)	21.1750 "	0.1385 "	0.1357 "	0.0028 "	+
(44)	21.0250 "	0.1369 "	0.1347 "	0.0022 "	+
(45)	20.8740 "	0.1357 "	0.1338 "	0.0019 "	+
(46)	21.0570 "	0.1383 "	0.1349 "	0.0034 "	+

In experiments (40) and (41), in which comparatively small amounts of titanium were employed, the separation from alumina was reasonably good after the second precipitation, but in (42) to (46) the larger quantities of titanic oxide still retained notable amounts of alumina. The precipitates of (45) and (46) were, therefore, treated again just as before, to determine the effect of a third precipitation.

	Weight of solution.	TiO_2 found (III).	TiO_2 by standard.	Error.	
(45)	20.8740 grm.	0.1347 grm.	0.1338 grm.	0.0009 grm.	+
(46)	21.0570 "	0.1360 "	0.1349 "	0.0011 "	+

Three precipitations left the titanic oxide of these experiments nearly free from alumina, but three such treatments involve a good deal of labor, and, moreover, it is evident that the precipitate still holds with tenacity traces of alumina. The experiment of attempting to remove residual alumina, after a single precipitation, by treating the product of fusion of the precipitate in sodic carbonate with boiling water, filtering, igniting the residue, again fusing with a little sodic carbonate, and proceeding from this point to dissolve in sulphuric acid and precipitate once more as before, was therefore tried, and the result is given in the record of (47) to (50).

	Weight of solution.	TiO_2 found.	TiO_2 by standard.	Error.	
(47)	20.8640 grm.	0.1329 grm.	0.1337 grm.	0.0008 grm.	—
(48)	21.1100 "	0.1345 "	0.1354 "	0.0009 "	—
(49)	20.9100 "	0.1332 "	0.1340 "	0.0008 "	—
(50)	21.0020 "	0.1348 "	0.1346 "	0.0002 "	+

This mode of treatment appears to remove the last traces of alumina and yields a reasonably good separation.

It appears therefore, to recapitulate, that for the separation of titanium and aluminum either of the processes set forth in the preceding work may serve. The first, however—which is, in brief, the treatment of the solution containing salts of the elements in question with a mixture of microcosmic salt and formic acid, in the proportion of two to three by weight, together with enough ammonic formate to take up the stronger acids, fusing the precipitate in sodic carbonate, extracting with water, fusing the residue in a small amount of sodic carbonate, dissolving in sulphuric acid and precipitating by ammonia with the subsequent addition of acetic acid, and boiling—though probably fairly accurate, is, on account of the nature of the precipitated phosphate, not comparable with the second method in point of convenience. The latter process, which involves many different manipulations—the introduction into the solution of titanium and aluminum of enough acetic acid to make from seven to eleven per cent. by volume of the absolute acid, together with sufficient sodic acetate to fix all of the stronger acids in sodium salts, boiling, filtering, and washing with acetic acid of 7% strength, fusing the ignited precipitate in sodic carbonate, extracting with boiling water, again fusing the residue with a little sodic carbonate, dissolving in strong sulphuric acid and pouring this solution into water, neutralizing with ammonia, redissolving the precipitate in a known amount of sulphuric acid, and precipitating finally by boiling with acetic acid and sodic acetate as at first—and appears in the description to be long and tedious, may in reality be carried out with ease and rapidity, the operations being generally short and not of a difficult nature.

In most cases in which titanium is to be separated from aluminum, it is necessary to effect the removal of iron as well. Some experiments looking to the separation of titanium and iron, by boiling the acetates in presence of a large excess of acetic acid, were unsuccessful; for, though an excess of acetic acid amounting to eleven per cent. of absolute acid in the solution is enough to prevent the deposition of a basic ferric acetate, it appears, unexpectedly, that in presence of ferric acetate in solution the titanium shows a very marked tendency to remain dissolved. Thus, an amount of iron alum the equivalent of 0.2 grm. of ferric oxide, together with 10 grm. of sodic acetate and seventeen per cent. of absolute acetic acid, in a total volume of 400 cm.^{3}, held 0.06 grm. of titanic oxide completely in solution during boiling prolonged a quarter of an hour. In an experiment the counterpart of this, excepting only the addition of sodic acetate, the titanium began to deposit at once on boiling; and Streit and Franz,[1] in proposing the ebullition of the sulphates in presence of a large excess of acetic acid as a means of procur-

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[1] Jour. prakt. Chem., CVIII, 65.

ing titanic oxide free from iron, claim a complete precipitation under these conditions. The behavior of the sulphates of titanium and zirconium when in solution together appears to be analogous to this action of the acetates of iron and titanium, and iron in the ferric condition is generally supposed to influence somewhat the precipitation of titanium from the solution of the sulphates.

When iron and titanium appear together in solution and are to be separated, the choice lies between Stromeyer's application of Chancel's hyposulphite method,[1] which yields milky filtrates—always undesirable—and that process which involves the precipitation of iron by ammonic sulphide in presence of ammonic tartrate to hold up the hydrates which would be precipitated in its absence. This latter method has been regarded as an undesirable one, chiefly on account of the inconvenience involved in the evaporation of the filtrate from the ferrous sulphide and the ignition of the residue to remove the tartaric acid, and so to permit the recovery of the bases. The difficulty in question may be obviated, however, by destroying the tartaric acid by potassic permanganate added gradually to the hot solution containing enough free sulphuric acid to leave some excess after the conversion of all the permanganate. The oxidation of tartaric acid by potassic permanganate does not, as is well known, yield carbonic acid and water alone, but gives rise also to a considerable quantity of formic acid as an intermediate product. When the permanganate begins to act upon the formic acid, the oxidation going on more slowly, results in the deposition of a brown manganic hydrate, which, if any tartaric acid remains in solution, redissolves quite rapidly, and, in presence of formic acid as the only reducing agent, more slowly. When, therefore, manganic hydrate is abundantly precipitated in the boiling solution and does not perceptibly dissolve, it is quite certain that the conversion of the tartaric acid to formic acid—which is all that is needed in this case—has been accomplished; but for the sake of greater security the addition of permanganate may be continued until its color shows in the solution. It is well, however, to make use in this process of a known amount of tartaric acid—experience has shown that an amount equal to three times the weight of the oxides to be held in solution is sufficient, unless ammonia be used in enormous excess and the boiling prolonged—and to employ for its destruction two and a half times its own weight of potassic permanganate, this quantity being more than enough to carry the oxidation to the final products, providing there were no deposition of manganic hydrate. The manganese thus introduced into the solution may be removed by two acetate precipitations, which, if alumina is to be separated, must be made at any rate, even if no manganese be present.

To separate titanium, aluminum, and iron, therefore, I find it most convenient to precipitate the iron by passing hydric sulphide into the

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[1] Ann. Ch. Pharm., CXIII, 127.

faintly ammoniacal solution of the oxides in ammonic tartrate, taking care that the solution is still ammoniacal just before filtering; to destroy the tartaric acid in the filtrate, after acidifying and boiling off the hydric sulphide by means of potassic permanganate in the manner just described, redissolving residual manganic hydrate by the addition of a little ammonic bisulphite and boiling off the excess of sulphurous acid; and to separate the titanium and aluminum by the acetate process.

A single point in the analysis of silicates may be worthy of note in this connection. If phosphoric acid be present, as is often the case, the separation of titanium from silica by the action of cold water upon the product of fusion in sodic or potassic bisulphate is liable to uncertainty, on account of the formation of the insoluble titanic phosphate which remains partly with the silica and in part clouds the filtrate. The silicious residue should, therefore, be treated with sulphuric and hydrofluoric acids to recover titanium which may be with the silica. It is better in most cases to effect the decomposition of a silicate by means of one of the fluoride methods or by fusion in an alkaline carbonate, the melt in the latter case being acidified with hydrochloric acid, and the residue after evaporation and filtration worked over with sulphuric and hydrofluoric acids for the recovery of that portion of the titanium which remains insoluble after the evaporation.

A METHOD OF FILTRATION BY MEANS OF EASILY SOLUBLE AND EASILY VOLATILE FILTERS.

By F. A. Gooch.

The processes of analysis in which it is desirable to redissolve precipitates from the filter after washing, or to separate a mixed precipitate into parts by the action of appropriate solvents, are many.

When a complete solution is the object and the precipitate yields easily to solvents which do not affect paper injuriously, the use of the ordinary filter offers no difficulty. When, however, precipitates are to be treated with reagents which disintegrate paper filters, the case is different; and the attempt to remove, by solvents, any individual part of a mixed heterogeneous mass upon a filter is always an uncertain matter. As examples of cases of this sort, difficult to deal with, we may take the solution of acid sodic titanate in strong hydrochloric acid; or, the purification of baric sulphate from included salts, by digestion in strong hydrochloric acid; or, the separation of sulphides which are soluble from those which are insoluble in alkaline sulphides; or, the washing out of free sulphur from precipitated sulphides by means of carbon disulphide; or, the separation of calcic and baric sulphates by the action of sodium hyposulphite. In cases of this nature it is often convenient to make use of the asbestus filter which I have previously described;[1] but this sometimes has its disadvantages. Thus, to recur to the examples just cited, acid sodium titanate may be filtered and washed upon an asbestus filter, and felt and precipitate may be treated together with hydrochloric acid, but it will be impossible to determine when solution is effected, because of the floating asbestus; and in separating the sulphides it would be necessary to know the weight of the asbestus felt, since it must be weighed finally with the insoluble sulphides, unless removed by a special treatment which involves the solution, filtration, and reprecipitation of the latter.

It is to meet cases like these that I have sought a filter which, in the reversal of the ordinary mode of separating filter and precipitate, should dissolve easily in solvents which do not affect the ordinary precipitates met with in analysis. The material which seems best suited to the case—light and fluffy, capable of making secure filters of any de-

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[1] Proc. Amer. Acad., Vol. XIII, p. 342.

sirable degree of porosity, sufficiently insoluble in water and aqueous solutions of salts, alkalies, and acids (excepting strong sulphuric, strong nitric, and glacial acetic acids), easily soluble in naphtha, benzol, carbon disulphide, ether, boiling alcohol, and essential oils, and not too costly—is anthracene.

The mode of preparing and using the filter is simple. Anthracene is slightly moistened with alcohol to make it miscible with water, diluted to the right consistency, and applied to the same apparatus, and in the same way, as the emulsion of asbestus which is employed in making asbestus felts. That is to say, enough of the emulsion in water to form a layer of the proper thickness is poured into a perforated crucible which is held tightly in a packing of rubber tubing stretched over a funnel fitted in the usual manner to a vacuum flask or receiver. After washing with water the filter is ready for use. If the felt happens to be too coarse for the use of the moment, it may be made as close as need be by coating the felt first deposited with a finer emulsion, made by dissolving anthracene in hot alcohol and precipitating with water. When voluminous precipitates are to be filtered, the large perforated cone described in the former paper, to which I have referred, may be substituted with advantage for the crucible; or Cooke's improved form[1] of Carmichael's process of reverse filtration may prove most useful. In using the cone it is well to apply the anthracene in a thick layer.

To remove the anthracene filter from a precipitate, it is only necessary to act with the proper solvent. It is usually convenient to stand the crucible containing precipitate and felt in a small beaker, add enough of the solvent, and gently warm until the anthracene dissolves. On the addition of water, or the reagent to work upon the precipitate, the solution of anthracene floats, and nothing remains to obstruct or obscure the action. If the precipitate dissolves entirely, the solution of anthracene may be separated from the aqueous solution by simply pouring the fluid upon a filter previously moistened with water, when the solution in water runs through, and the anthracene and its solvent remain and may be washed indefinitely with water.

If, on the other hand, the case is one of the division of precipitates, the anthracene and its solvent may be made to pass the filter, after the water has run through, by adding a little alcohol to overcome the repulsion between the solution and the water which fills the pores of the filter, the precipitate which stays behind being washed first with a solvent of anthracene, and then, if necessary, with alcohol followed by water; or, if the vacuum filter be used (either paper or asbestus, according to the circumstances of the case), both liquids leave the precipitate and traverse the filter together.

In general, I prefer benzol as the solvent for anthracene, but some advantage may be gained in special cases by a proper choice of solv-

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[1] Proc. Amer. Acad., Vol. XII, p. 124.

ents. Thus, in removing intermixed sulphur from precipitated sulphides, both the anthracene and the sulphur may be dissolved in carbon-disulphide in a single operation.

The ready volatility of anthracene, at a temperature very near its melting point, 213° C., makes it easily separable in cases when to remove it by a solvent is not advisable. The treatment of a solution of anthracene, for example, with strong sulphuric or nitric acid, is apt to produce carbonaceous or gummy residues. In such cases it is well either to heat precipitate and filter directly, or to first remove them from the crucible by means of a solvent for anthracene, then evaporate this and raise the heat gently until the anthracene has vanished. The purification of precipitated baric sulphate, by dissolving it in hot, strong sulphuric acid, and reprecipitating by dilution, is a case in point, and one, too, in which the reversed filter may be used with great advantage. It may be remarked, in passing, that, if one does not happen to possess a platinum rose and does happen to have at disposal a perforated crucible, a very fair reversed filter may be improvised of the crucible, a piece of glass tubing, and a rubber stopper, the last being fitted to the crucible and the tube passed through nearly to the perforated bottom.

At every point in the preparation and use of the anthracene filter, I have found the manipulation peculiarly easy.

THE RELATION BETWEEN ELECTRICAL RESISTANCE AND DENSITY, WHEN VARYING WITH THE TEMPER OF STEEL.

By C. Barus and V. Strouhal.

EXPERIMENTAL RESULTS.

Introductory.—Throughout No. 14 of the series of Bulletins of the United States Geological Survey it was our constant endeavor to keep before the mind certain lines of electrical research, such as would immediately advance our knowledge of the influence of the mechanical condition of steel on its electrical and magnetic qualities. We pointed out, in particular, the urgency of a minute study of the change of density experienced by steel on passing from hard to soft, as well as the critical importance of the nature and variation of the internal structure of a tempered bar. We called attention to our ignorance of many essential features of the process by which hardness is imparted and of the conditions subject to which hardness is received. We attempted to supply a more rigid interpretation for the magnetic relations of linear rods and for the temper-datum of the oxide films.

To most of these points we have since been able to give more or less attention, although only the small part referring to the density and conductivity of steel is sufficiently in progress to deserve special mention here.

Tempering.—In making the present measurements we used Stubs' best steel, furnished by Mr. William Grunow, of West Point. The rods are about a foot in length, and drawn very accurately circular, a desideratum. They were tempered in a way essentially the same as that employed in all our researches. We found it expedient, however, to modify the apparatus for glass-hardening in a way enabling the experimenter to work with much greater facility and expedition, as well as to quench (chill) in baths of any desirable temperature. It will be described elsewhere. We will mention in passing that the sections of our steel rods, before and after tempering, were found to differ in marked degree; that the sense of this difference is precisely the opposite of the effect to be attributed to temper. Certain incidental gravimetric measurements, for instance, showed the following results:

TABLE 1.—*Certain gravimetric measurements of section (q), soft and glass-hard.*

Number.		Soft.	Hard.	
37–54	$q=$	0.001537	....	(Thin.)
30–36	$q=$	0.005231	0.005162	(Intermediate.)
55–60	$q=$	0.01268	0.01257	(Thick.)

The actual effect of temper is here a diminution of the sectional area; the anticipative effect would be an increment of about twice the amount (Cf. Table 14). This anomalous result is probably attributable to the tensile strain under which the wires are glass-hardened. It is not easily avoided.

Earlier results.—Values for the electrical resistance of steel will be found in great number in the bulletin cited, and the mean results of these we will frequently be able to utilize with advantage in the present text. Results for the density of steel when in the extreme states, hard and soft, are also available in any number and for every variety of steel. But Dr. Fromme[1] seems to have been the first and indeed the only observer who attempted to trace the change of density of steel passing *continuously* from the initial state of temper to the final state. We give his summarized results in Table 2, where ρ denotes the radius in centimeters, v the specific volume of the rods examined. For the sake of clearness in comparison, we add, moreover, the probable mean values of electrical resistance characteristic of the different states of temper under consideration. In doing this we remark that the loci thus obtained, though not strictly correct ("dispersed"), will exhibit the main features of the true diagram in about the same way in which the fundamental characteristics of the solar spectrum may be shown by a number of different prisms, no two spectra, however, being exactly alike.

TABLE 2.—*Dr. Fromme's results for specific volume (v), for different diameters (2ρ), with approximate electrical resistances (s) added.*

Temper.	$2\rho=0.7$ v	$2\rho=0.42$ v	$2\rho=0.265$ v	$2\rho=0.255$ v	Mean s
Commercial, soft	1.00000	1.00000	1.00000	1.00000	....
Hard	1.00772	1.01000	1.01285	1.01210	(46)
Yellow-annealed	1.00347	1.00495	1.00660	1.00620	(26)
Blue-annealed	1.00217	1.00425	1.00370	1.00205	(20)
Gray-annealed	0.99957	1.00060	1.00055	0.99930	(18)
Soft	....	1.00175	1.00215	1.00340	(16)

In endeavoring to interpret these results we encounter a serious difficulty in consequence of the absence of a sufficient number of intermediate points. But anticipating certain results below and restricting

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[1] C. Fromme: Wied. Ann., VIII, p. 352, 1879.

our observations for the present to the data between "*hard*" and "*gray annealed*," we find all the points lying on curves of remarkably definite character. Even closer agreement is apparent in the results for thin rods and in the results for thicker rods. Indeed, it is only necessary to shift the values for specific resistance through a small interval—an interval insufficiently large to comprehend the electrical behavior of good commercial steels for the same states—in order to obtain loci of very simple kind. We show below that, even in the case of an elementary linear relation between volume and resistance—such, for instance, as approximately holds for thermal expansions—the simple law, in case of structural heterogeneity, may lead in the aggregate to very complex results.

Fromme's data, however, contain a remarkable and almost anomalous phenomenon, viz, expansion of volume on passing from "*gray*" to "*soft*." This implies a march through a maximum of density somewhere between these two limiting states. The peculiar behavior in question, when associated with Chwolson's[1] discovery of a minimum of resistance of steel, and our results on the maximum of magnetizability—all which phenomena occur under like circumstances of temper, approximately—lead us to attach great importance to the precise definition of this singular state.

Finally, the inferences, which in this paragraph are only touched upon, are not dependent on merely qualitative analogies. They are often strikingly substantiated by estimates obtainable from a variety of known quantitative results. It is curious that this variation, which draws into close affinity an electrical function and one of the simplest mechanical functions of the physical state of steel, has not hitherto been made the subject of more searching investigation. If, as we surmise, the electrical manifestations of hardness may be regarded independent of any chemical change which steel during tempering undergoes, it would seem that the relation between volume and resistance is at once raised to higher and more general importance than that of being a mere peculiarity of steel.

Difficulties of measurement.—An accurate measurement of the simultaneous variations of resistance and density is experimentally difficult. The change of density due to the tempering of steel lies well within 2 per cent. To measure this small increment with an accuracy of 1 per cent. necessitates a measurement of the total density to within 0.02 per cent. This is readily feasible, provided the given sample is sufficiently large and of convenient shape. From such a piece,[2] however, it would be impossible to measure the electrical quality with any serviceable degree of accuracy whatever. For resistance measurement it is necessary to have the material in wire form,[3] *i. e.*, to give it precisely the

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[1] Chwolson: Mél. Phys. de St. Pétersbourg, X, p. 379, 1877.

[2] Kirchhoff's and other methods require special apparatus.

[3] In the proposed magnetic experiments the use of linear rods is essential; moreover, such alone can be hardened homogeneously.

shape least adapted for desirably accurate density measurements. Reasons of this kind at first induced us to doubt the satisfactory feasibility of the present series of correlative measurements. The results show that the determinations can well be made.

Measurement of density.—In our early experiments we used a direct method for density measurement, employing a balance counterpoise with a lateral arm so adjusted as to swing the long (30 cm.) thin wire from a silk fiber in a stand-glass of water. But the results obtained were not reliable within 0.1 per cent. The pycnometer, therefore, is the only apparatus available for the present purposes. The mean constants of the flasks and of the capillary stems of the pycnometers used follow:

TABLE 3.—*Mean constants of the pycnometers.*

	No. 2.	No. 3.	No. 4.
Total weight ....grm..	5.43	5.67	5.47
Total capacity, H_2O ....grm..	3.51	3.39	3.64
Flask (cylindrical):			
Height ....cm..	3	3	3
Diameter, external ....cm..	1.3	1.3	1.3
Capillary stem:			
Internal diameter of the tube ....cm..	0.030	0.032	0.030
Mass H_2O, per cm ....grm..	0.00070	0.00079	0.00070
Temperature H_2O, per cm., at 25°	0°.80	0°.93	0°.77

The hard wires were so broken and were used in such quantity as almost wholly to fill the flask. Having filled it with water at room temperature, we allowed it to stand in the balance-case until the position of the meniscus became fixed. The weight was now taken and the operation repeated after the lapse of one hour or more. The temperature could then be regarded as identical with the value read off on a good mercurial thermometer placed almost in contact with the pycnometer, provided, of course, neither the temperature of the balance-case nor the height of the meniscus had varied during this interval. The rate of evaporation through so fine a capillary tube is practically nil. This is shown in Table 4, where pycnometer weights for different times are recorded.

TABLE 4.—*Rate of evaporation (transpiration) through capillary stems of the pycnometers.*

Time	$9^h\ 0^m$	$9^h\ 30^m$	$10^h\ 10^m$	$12^h\ 0^m$	$1^h\ 0^m$	$1^h\ 0^m$	$2^h\ 20^m$
Meniscus	2.20	2.15	2.15	2.30	2.30	1.90	2.10
Weight of pycnometer.......	16.25622	16.25630	16.25622	16.25625	16.25622	16.25560	16.25558

These pycnometers were, therefore, virtually thermometers, and 1 cm. of the stem of the instrument used corresponded to about a degree. Great care must be taken to have the stem thoroughly well ground into the neck of the flask; otherwise water escapes here at a rate sufficiently large to vitiate the present method of measurement. The stopper-error, finally, is so small that where a room of constant temperature is available the results may be relied upon to a few one-thousandths per cent. When temperature fluctuates, as in an ordinary room, the accuracy decreases rapidly to a few one-hundredths per cent.

In operating with iron and steel a source of error is introduced by the fact that the wires are liable to rust.[1] The pycnometer soon shows the yellow color of the hydrate. It is necessary, therefore, not only to rinse the apparatus frequently with hydrochloric acid, but to scour the wire with fine emery paper before each measurement. When so many as 70 wires come to a batch this is excessively tedious, but nevertheless unavoidable. Frequent rinsing with ether is also desirable to remove particles of grease which may collect in the flask.[2]

In the tables, Δ_0 denotes the density of steel at 0° centigrade, v_0 the corresponding volume of the unit of mass.

Measurement of resistance.—To measure the resistances of the short lengths of wire (3 cm.) we constructed an especial apparatus based on Matthiessen and Hockins' principle. A series of folding parallel arms pressed the pieces of steel firmly down upon flat plates of brass properly connected with a bridge. Resistances of constant lengths were always taken with results correct to 1 per cent. Further description of the apparatus and method will be given later.

In the tables the resistance between opposite faces of a cubic centimeter, in microhms, at 0° C., will be denoted by s_0.

To co-ordinate the values for resistance and density—*i. e.*, in order to obtain pairs of data referable, as it were, to the same steel rod—we proceeded thus: The central piece (3 cm.) of the homogeneous portion of each rod was reserved for the resistance measurement; the remainder of the rod furnished the pieces for the density measurement. During the annealing all the pieces were exposed in like manner. In the case of thin rods this method becomes very tedious; for instance, when operating with rods Nos. 21–29, it was necessary to break 9 rods, of 30 cm. each, in order to obtain sufficient material for the density work. Nine measurements of resistance were therefore to be made for each measurement of density; our reasons for avoiding the use of very fine steel wire are therefore apparent.

Method of annealing.—At low temperatures ($<400°$), the usual vapor and metallic baths were used for annealing; at high temperatures, the steel wires were either exposed in an "annealer" or other similar processes were resorted to. The "annealer" is a T-shaped apparatus made of gas-pipe, with a very short horizontal (9 cm.) but long vertical shank (37 cm.). The wires to be annealed, after having been wrapped in many layers of copper foil, or at very high temperatures in platinum foil, alternating with layers of iron wire, are symmetrically introduced into the former (short) shank. This is then closed by a screw-cap at each end. All waste space is filled with iron filings. Into the vertical shank we inserted an insulated thermo-element of known constants, so adjusted

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[1] The use of liquids other than water is not advisable.

[2] The cautious use of grease in fitting stopper to flask is indispensable.

that the hot junction just touched the fascicle of steel wires. To insure slow heating and cooling, we surrounded the T of the "annealer" by a layer of carded asbestus (5 cm. thick), and then heated it to the desired temperature in a muffle furnace. The object of the whole arrangement is to *avoid oxidation* as much as possible during the annealing.[1] In the apparatus used, bright steel heated for one hour at white heat remained bright. The accurately circular section of the wires was therefore never sacrificed by the exposure. In one instance where the temperature was accidentally chosen so high as to fuse the copper envelope, this was sucked up into the capillary interstices between the wires, forming a mass which, after cooling, was soldered throughout and compact. For our highest temperatures it was not expedient to use the "annealer." The wires were then wrapped in asbestus paper and heated in a closed crucible filled with iron filings. In these cases slight oxidation was unavoidable. We therefore carefully removed the surface and repolished the wires before each measurement.

Experimental results.—Tables 5 and 6 of the following series contain the results of introductory experiments. They were obtained by a direct process, the large masses of steel being weighed in water. l expresses the length, ρ the radius, μ the mass of the cylinders employed. The density, Δ_t, was observed at t°; Δ_0, and the specific volume v_0, are calculated for 0° C.

TABLE 5.—*Density of rod No. I. Direct method.*

[l=5.35 cm. ρ=0.95 cm.]

μ	Temper.	t	Δ_t	Δ_0	Mean Δ_0	v_0	Remarks.
119.9336	Commercial, soft..........	° 18.1 18.4	7.8325 7.8318	7.8375 7.8368	7.8372	0.12760	
119.6381	Glass hard, 25°, ∞	14.7 15.6	7.8050 7.8046	7.8092 7.8091	7.8092	0.12805	
119.5820	Annealed, 100°, 1^h (steam).	17.7	7.8038	7.8088	7.8088	0.12806	
119.5759	Annealed, 100°, 4^h (steam).	23.5 23.8	7.8030 7.8028	7.8095 7.8094	7.8094	0.12805	
119.5683	Annealed, 100°, 8^h (steam).	17.4 16.5	7.8059 7.8062	7.8108 7.8108	7.8108	0.12803	
119.5676	Annealed, 100°, 12^h (steam)	23.3	7.8049	7.8114	7.8114	0.12802	
119.5662	Annealed, 200°, 30^m (camphor).	24.7 24.7	7.8028 7.8025	7.8097 7.8094	7.8096	0.12805	This and the following observations made 2½ years after the above.
119.5140	Annealed, 330°, 5^m (lead) ..	23.8 23.8	7.8168 7.8171	7.8234 7.8237	7.8236	0.12782	
119.3952	Annealed, 620°, 5^m (lead) ..	24.1 24.1	7.8277 7.8275	7.8343 7.8341	7.8342	0.12765	Rod not covered during exposure.
118.4945	Annealed, 805°, 30^m (lead) .	20.9 21.0	7.8297 7.8309	7.8355 7.8367	7.8361	0.12762	Rod wrapped in asbestus paper during exposure.
117.8363	Annealed (1,300°)	21.0 21.3	7.8406 7.8409	7.8464 7.8467	7.8465	0.12744	Rod wrapped in asbestus paper, surrounded with iron filings, exposed in closed crucible.

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[1] The method of wrapping up the sample in foil we owe to Kohlrausch.

TABLE 6.—*Density of rod No. II. Direct method.*

[l=10.11 cm.; ρ=0.288 cm.]

μ	Temper.	t	Δ_t	Δ_0	Mean Δ_0	v_0	Remarks.
20.0971	Commercial, soft	° 19.6	7.6979	7.7033	7.7033	0.12981	
20.0348	Glass hard, 25°, ∞	19.0 19.6	7.6144 7.6147	7.6197 7.6202	7.6200	0.13123	
20.0330	Annealed, 190°, 4^m (aniline)	25.2 25.3	7.6470 7.6476	7.6539 7.6545	7.6542	0.13065	
20.0268	Annealed, 330°, 2^m (lead)	25.0 25.0	7.6586 7.6598	7.6655 7.6667	7.6661	0.13044	
19.9674	Annealed, 645° (lead)	21.4 21.5	7.6967 7.6933	7.7025 7.6991	7.7008	0.12986	Rod wrapped in asbestus paper during exposure.
19.8476	Annealed, 830° (lead)	22.1 22.2	7.7111 7.7108	7.7172 7.7169	7.7170	0.12958	Do.
19.2113	Annealed (1,300°)	22.0 22.1	7.7326 7.7337	7.7387 7.7398	7.7392	0.12922	Rod wrapped in asbestus paper, surrounded with iron filings, exposed in a closed crucible.

In Tables 7, 9, 11 the densities (Δ_t, Δ_0) contained were determined by the aid of the pycnometers above described. In other respects the remarks made with reference to Tables 5 and 6 apply here. q is used as the symbol of section. $q\,(s)$ denotes the section of the rod when soft, $q\,(h)$ the section of the same rod hard. The temper was imparted by heating with the electric current and then quenching (p. 30).

Tables 8, 10, 12 contain values for specific resistance s, and correspond to Tables 7, 9, 11, respectively. s_t is observed at t^0; s_0 calculated for 0° C. by aid of the coefficient α. The column r_t, finally, shows the resistance in microhms per centimeter of wire.

We may remark that rods Nos. 21 to 29 and Nos. 30 to 36, rods Nos. 55 to 60 and Nos. 61 to 63, are of like kind and origin.

TABLE 7.—*Density of the rods Nos.* 61 *to* 63. *Pycnometer.*

[Twenty-one pieces: $q_0\,(s)=0.01268$; $q_0\,(h)=0.01257$. Mean $l=2.5$ cm.; mean $\rho=0.0634$ cm.]

μ	Temper.	t	Δ_t	Δ_0	Mean Δ_0	v_0	Remarks.
11.8068	Commercial, soft	° 24.1 24.0	7.7227 7.7315	7.7293 7.7381	7.7337	0.12931	Data obtained with Nos. 55–60.
6.2323	Glass hard, 25°, ∞	26.1 26.0	7.6610 7.6622	7.6682 7.6694	7.6688	0.13040	
6 2301	Annealed, 100°, 9^h (steam)	27.4 27.5	7.6821 7.6981	7.6896 7.7056	7.6976	0.12991	
6.2293	Annealed, 200°, 2^m (paraffine).	24.6 24.8	7.6934 7.6890	7.7003 7.6959	7.6981	0.12990	
6.2289	Annealed, 200°, 30^m (camphor).	23.2 23.5	7.6964 7.6969	7.7028 7.7033	7.7030	0.12982	
6.2274	Annealed, 330°, 30^m (lead)	23.4 23.5 23.8	7.7103 7.7228 7.7117	7.7168 7.7293 7.7183	7.7215	0.12951	Wires in the annealer.

TABLE 7.—*Density of the rods Nos.* 61 *to* 63. *Pycnometer*—Continued.

μ	Temper.	t	Δ_t	Δ_0	Mean Δ_0	v_0	Remarks.
		°					
6.2215	Annealed, 810°, 30^m (lead).	24.3	7.7798	7.7864	7.7872	0.12842	Wires in the annealer.
		24.5	7.7815	7.7881			
6.2140	Annealed (1,000°)	24.4	7.7818	7.7884	7.7865	0.12843	Wires in the annealer cooled quick from the high temperature.
		24.6	7.7779	7.7845			
6.2085	Annealed (1,300°)	25.1	7.7933	7.8002	7.8007	0.12819	Wires in asbestus paper, surrounded with iron filings, exposed in a closed crucible.
		25.1	7.7943	7.8012			

TABLE 8.—***Specific resistances of the rods Nos.*** **61 *to* 63, *corresponding to the above values,*** *Table* 7.

Nos.	Temper.	r_t	t	s_t	a	s_0	Mean s_0.
			°				
55 to 60	**Commercial, soft ....**	1,330	26	16.8	0.0038	15.2	15.25
		1,340	26	16.9	38	15.3	
		1,330	26	16.8	38	15.2	
61 to 63	**Glass-hard, 25°, ∞ ....**	3,590	26	45.3	0.0016	43.6	43.29
		3,560	26	44.9	16	43.2	
		3,540	26	44.6	16	43.0	
61 to 63	**Annealed, 100°, 9^h ....**	2,960	28	37.4	0.0019	35.6	35.61
		2,950	28	37.3	19	35.5	
		2,970	28	37.5	19	35.7	
61 to 63	**Annealed, 200°, 2^m...........**	2,750	22	34.7	0.0021	33.2	33.11
		2,740	22	34.6	21	33.1	
		2,730	22	34.5	21	33.0	
61 to 63	**Annealed, 200°, 30^m..........**	2,420	23	30.6	0.0024	29.0	28.76
		2,380	23	30.1	24	28.5	
		2,400	23	30.3	24	28.8	
61 to 63	**Annealed, 330°, 30^m..........**	1,760	24	22.3	0.0032	20.6	20.61
		1,760	24	22.3	32	20.6	
		1,750	24	22.2	32	20.5	
61 to 63	**Annealed, 810°, 30^m..........**	1,570	25	19.8	0.0034	18.2	18.10
		1,560	25	19.7	34	18.1	
		1,550	25	19.6	34	18.0	
61 to 63	**Annealed (1,000°)...........**	1,670	24	21.2	0.0033	19.6	19.74
		1,680	24	21.3	33	19.7	
		1,700	24	21.5	33	19.9	
61 to 63	**Annealed (1,300°)...........**	1,680	25	21.2	0.0033	19.6	19.29
		1,640	25	20.7	33	19.1	
		1,640	25	20.7	33	19.1	

TABLE 9.—*Density of the rods Nos.* 0.

[Eighteen pieces: $q_0\ (s)=0.03904$; $q_0\ (h)=0.03955$. Mean, $l=3.0$ cm.; mean, $\rho=0.112$ cm.]

μ	Temper.	t	Δ_t	Δ_0	Mean Δ_0	v_0	Remarks.
25.2323	Commercial, soft	° 21.0	7.806	7.812	7.812	0.12801	Early value. Large pycnometer used.
14.3778	Glass hard, 25°, ∞	20.8 20.8	7.6759 7.6759	7.6817 7.6817	7.6817	0.13018	19 pieces.
13.7039	Annealed, 100°, 10^m (steam)	25.1 25.5	7.6881 7.6867	7.6950 7.6938	7.6943	0.12997	18 pieces.
—	Annealed, 100°, 7^h (steam)	25.6 26.0	7.7032 7.7027	7.7104 7.7099	7.7102	0.12970	
13.6984	Annealed, 190°, 15^m (aniline)	26.1 26.3	7.7172 7.7186	7.7244 7.7258	7.7251	0.12945	
13.6966	Annealed, 330°, 8^m (lead)	26.1 25.9	7.7348 7.7390	7.7420 7.7462	7.7441	0.12913	
13.6927	Annealed, 460°, 1^h (lead)	24.5 24.4	7.7570 7.7576	7.7638 7.7644	7.7641	0.12880	Wires in the annealer.
13.6773	Annealed, 720°	24.6 24.7	7.7720 7.7729	7.7789 7.7798	7.7793	0.12854	Wires in the annealer. Copper foil.
13.6682	Annealed (900°)	26.9 27.2 27.3	7.7733 7.7808 7.7756	7.7808 7.7883 7.7831	7.7840	0.12846	Do.
13.5855	Annealed (1,100°)	28.3 28.1 28.2	7.7768 7.7820 7.7773	7.7846 7.7898 7.7851	7.7865	0.12843	Wires in the annealer. Platinum foil.
13.5636	Annealed (1,300°)	25.2 25.3	7.7781 7.7793	7.7862 7.7850	7.7856	0.12844	Wires wrapped in platinum foil, surrounded with iron filings exposed in a closed crucible.

TABLE 10.—*Specific resistances of the rods Nos.* 0, *corresponding to the above values, Table* 9.

Temper.	r_t	t	s_t.	a	s_0.	Mean s_0.
Annealed, 460, 1^h	502 502 493	° 27 27 27	20.1 20.1 19.8	0.0034 34 34	18.4 18.4 18.0	18.27
Annealed, 720°	471 462 462	24 24 24	18.9 18.5 18.5	0.0035 35 35	17.4 17.0 17.0	17.13
Annealed, 900°	499 490 490	28 28 28	20.0 19.7 19.7	0.0034 34 34	18.3 18.0 18.0	18.10
Annealed, 1,100°	510 510 501	28 28 28	20.5 20.5 20.1	0.0034 34 34	18.7 18.7 18.4	18.60
Annealed, 1,300°	501 510 474	25 25 25	20.1 20.5 19.0	0.0033 33 33	18.5 18.9 17.5	18.30

TABLE 11.—*Density of the rods Nos.* 21 *to* 29. *Pycnometer.*

[Seventy-two pieces: $q_0\ (s) = 0.00523$; $q_0\ (h) = 0.00516$. Mean, $l = 2.5$ cm.; mean, $\rho = 0.0407$ cm.]

μ	Temper.	t	Δ_t	Δ_0	Mean Δ_0	v_0	Remarks.
7.4670	Commercial, soft	25.9°	7.7177	7.7249	7.7268	0.12942	Nos. 30–36.
		25.6	7.7215	7.7287			
8.4014	Glass hard, 25°, ∞	25.3	7.6472	7.6540	7.6547	0.13064	
		26.3	7.6490	7.6561			
		27.5	7.6467	7.6540			
8.4014	Annealed, 100°, 1^h (steam)	29.3	7.6576	7.6656	7.6666	0.13044	
		29.8	7.6575	7.6658			
		28.9	7.6605	7.6685			
		30.0	7.6581	7.6664			
	Annealed, 100°, 13^h (steam)	25.0	7.6677	7.6746	7.6745	0.13030	
		25.4	7.6676	7.6745			
8.4001	Annealed, 190°, 40^m (aniline)	26.8	7.6770	7.6845	7.6841	0.13014	
		26.9	7.6761	7.6836			
8.3993	Annealed, 190°, 3^h 30^m (aniline).	26.4	7.6733	7.6808	7.6808	0.13020	72 pieces.
8.2811		27.1	7.6670	7.6745	7.6748	0.13030	71 pieces, one rod lost.
——		27.4	7.6695	7.6770			
8.2819		27.4	7.6655	7.6730			
8.2812 8.2815	Annealed, 330°, 10^m (lead)	27.6	7.6737	7.6813	7.6806	0.13020	Wires in the annealer.
		27.4	7.6701	7.6800			
8.2807	Annealed, 470° (lead)	25.0	7.7123	7.7192	7.7190	0.12955	Do.
		25.2	7.7119	7.7188			
8.2829	Annealed, 530° (lead)	26.0	7.7160	7.7232	7.7227	0.12949	Do.
		25.9	7.7149	7.7221			
8.2848	Annealed, 690°	24.3	7.7210	7.7276	7.7272	0.12941	Wires in the annealer. Quick cooling.
		24.0	7.7201	7.7267			
8.2705 8.2519	Annealed, 810°	25.5	7.7509	7.7579	7.7586	0.12889	Wires in the annealer; copper foil; slower cooling.
		25.5	7.7540	7.7610			
		25.6	7.7500	7.7570			
8.2445	Annealed, 1000°	25.4	7.7612	7.7682	7.7705	0.12869	Wires in the annealer; copper foil; slower cooling; weight decreases without perceptible oxidation.
		25.3	7.7629	7.7699			
		25.5	7.7640	7.7710			

TABLE 12.—*Specific resistances of the rods Nos.* 21 *to* 29, *corresponding to the above values, Table* 11.

Nos.	Temper.	r_t	t	s_t	a	s_0	Mean s_0.
			°				
30 to 36	Commercial, soft	3,458	22	17.8	0.0036	16.5	16.27
		3,415	22	17.6	36	16.3	
		3,405	22	17.6	36	16.2	
21 to 23	Glasshard, 25°, ∞	8,988	27	46.4	0.0016	44.5	43.86
		8,896	27	45.9	16	44.1	
		8,750	27	45.1	16	43.4	
24 to 26	......do	9,116	27	47.0	15	45.3	
		9,062	27	46.8	15	45.0	
		8,614	27	44.4	17	42.6	
27 to 29	......do	8,738	27	45.1	16	43.3	
		8,738	27	45.1	16	43.3	
		8,724	27	45.0	16	43.2	
21 to 23	Annealed, 100°, 1h	8,162	31	42.1	0.0017	40.1	39.26
		8,013	31	41.4	18	39.3	
		7,890	31	40.7	18	38.7	
24 to 26	......do	8,258	30	42.6	17	40.7	
		8,234	30	42.5	17	40.6	
		7,763	30	40.1	18	38.1	
27 to 29	......do	7,901	30	40.8	18	38.8	
		7,863	30	40.6	18	38.6	
		7,825	30	40.4	18	38.4	
21 to 23	Annealed, 100°, 13h..........	7,392	24	38.2	0.0019	36.6	35.51
		7,238	24	37.4	19	35.9	
		7,062	24	36.4	20	34.9	
24 to 26	......do	7,485	25	38.6	19	37.1	
		7,385	25	38.1	19	36.6	
		6,965	25	35.9	20	34.4	
27 to 29	......do	7,057	26	36.4	20	34.8	
		7,057	26	36.4	20	34.8	
		6,993	26	36.1	20	34.5	
21 to 23	Annealed, 190°, 40m..........	6,427	27	33.2	0.0021	31.6	30.82
		6,301	27	32.5	22	30.9	
		6,174	27	31.9	22	30.3	
24 to 26	......do	6,584	27	34.0	21	32.4	
		6,503	27	33.6	21	32.0	
		6,145	27	31.7	22	30.1	
27 to 29	......do	6,159	27	31.8	22	30.2	
		6,124	27	31.6	22	30.0	
		6,112	27	31.5	22	30.0	
21 to 23	Annealed, 190°, 3h, 30m.....	5,707	28	29.5	0.0025	27.5	27.10
		5,617	28	29.0	25	27.1	
		5,494	28	28.4	26	26.4	
24 to 26	......do	5,942	27	30.7	23	28.8	
		5,800	27	29.9	24	28.1	
		5,471	27	28.2	26	26.3	
27 to 29	......do	5,536	27	28.6	25	26.7	
		5,512	27	28.4	26	26.6	
		5,450	27	28.1	26	26.3	
21 to 23	Annealed, 330°, 10m.........	4,361	27	22.5	0.0032	20.6	
		4,328	27	22.3	32	20.5	
		4,296	27	22.2	32	20.3	

TABLE 12.—*Specific resistances of the rods Nos.* 21 *to* 29, *&c.*—Continued.

Nos.	Temper.	r_t	t °	s_t	α	s_0	Mean s
24 to 26	Annealed, 330°, 10^m	4,539	28	23.4	31	21.5	20.68
		4,419	28	23.2	31	21.3	
		4,295	28	22.2	32	20.3	
27 to 29	do	4,376	28	22.6	32	20.7	
		4,365	28	22.5	32	20.6	
		4,308	28	22.2	32	20.4	
21 to 23	Annealed, 470°	3,883	25	20.0	0.0034	18.4	18.36
		3,873	25	20.0	34	18.3	
		3,831	25	19.8	34	18.1	
24 to 26	do	4,057	26	20.9	33	19.2	
		4,003	26	20.7	33	18.9	
		3,842	26	19.8	34	18.2	
27 to 29	do	3,922	26	20.2	34	18.5	
		3,900	26	20.1	34	18.4	
		3,847	26	19.8	34	18.2	
21 to 23	Annealed, 530°	3,809	25	19.7	0.0034	18.1	18.17
		3,789	25	19.6	34	18.0	
		3,737	25	19.3	35	17.7	
24 to 26	do	4,052	25	20.9	33	19.3	
		3,924	25	20.3	34	18.6	
		3,732	25	19.3	35	17.7	
27 to 29	do	3,845	25	19.8	34	18.2	
		3,813	25	19.7	34	18.1	
		3,781	25	19.5	34	17.9	
21 to 23	Annealed, 690°	3,630	25	18.7	0.0035	17.2	17.24
		3,589	25	18.5	35	17.0	
		3,548	25	18.3	36	16.7	
24 to 26	do	3,847	25	19.9	34	18.2	
		3,759	25	19.4	35	17.8	
		3,507	25	18.1	36	16.5	
27 to 29	do	3,686	25	19.0	35	17.4	
		3,654	25	18.9	35	17.3	
		3,580	25	18.5	35	16.9	
21 to 23	Annealed, 810°	3,686	26	19.0	0.0035	17.4	17.56
		3,676	26	19.0	35	17.3	
		3,646	26	18.8	35	17.2	
24 to 26	do	3,882	26	20.0	34	18.3	
		3,841	26	19.8	34	18.2	
		3,643	26	18.8	35	17.2	
27 to 29	do	3,738	26	19.3	35	17.6	
		3,696	26	19.1	35	17.4	
		3,696	26	19.1	35	17.4	
21 to 23	Annealed, 1,000°	3,935	25	20.3	0.0034	18.7	18.59
		3,903	25	20.1	34	18.5	
		3,862	25	19.9	34	18.3	
24 to 26	do	4,069	25	21.0	33	19.4	
		4,016	25	20.7	33	19.1	
		3,889	25	20.1	34	18.5	
27 to 29	do	3,923	25	20.2	34	18.6	
		3,860	25	19.9	34	18.3	
		3,785	25	19.5	34	18.0	
21 to 29	Annealed, *1,170°						

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*Fusion of the copper envelope destroys the wires.

In view of the curious increase of resistance observed in wires annealed at high temperatures ($>800°$)—an increase unaccompanied by a corresponding change in the sign of the density-effect, and under no circumstances attributable to variation of section—we thought it desirable to make a series of special *direct* comparisons between steel wires so annealed and wires of the same kind in the commercial soft state. All constants, including the sections of the individual wires, were measured anew. We give the data in Table 13, adding also the earlier values for q_0 and s_0 contained in the tables above. Mere inspection of Table 13 shows that the difference between the present and the early values of s_0, after allowing for the different values of q involved, are wholly within the unavoidable errors of observation. The two sets of data are therefore in good accordance.

TABLE 13.—*Direct comparison of resistances, "soft" (Nos.* 61 *to* 63) *and "commercial, soft" (Nos.* 55 *to* 60).

[Nos. 61 to 63, $\rho = 0.0634$ cm.; $q = 0.01263$. Nos. 55 to 60, $\rho = 0.0635$ cm.; $q = 0.01266$.]

Nos.	Temper.	r_t	s_t	t	a	s_0	Mean s_0	Early values.*	
								s_0	q
				°					
61 to 63.	Annealed (1,300°), cooled slowly.	1, 648	20. 80	26	0. 0033	19. 18	19. 13	19. 3	0. 01263
		1, 638	20. 68	26	33	19. 07			
		1, 645	20. 76	26	33	19. 15			
55 to 60.	Commercial, soft............	1, 349	17. 09	26	0. 0038	15. 54	15. 52	15. 3	0. 01263
		1, 362	17. 26	26	38	15. 68			
		1, 333	16. 88	26	38	15. 35			

* Date of present values: September 3, 1885; date of early values: June 30, 1885.

In Table 14 we cite certain special results for the diameters of wires No. 0 in the glass-hard state and after softening. The differences are readily accounted for, being referable to the volume-increase due to tempering. The diminution of diameter due to oxidation must therefore be less than 0.2 per cent.

TABLE 14.—*Diameters* (2ρ) *of the rods Nos.* 0, *glass hard and soft.*

	2ρ	2ρ	2ρ	Mean 2ρ.
Glass hard..cm..	0. 2250	0. 2240	0. 2240	0. 2243
After annealing at white heat (1,300°)....................cm..	0. 2230	0. 2224	0. 2234	0. 2229
Sections calculated (Table 16)..........................cm..	0. 2238	0. 2228	0. 2228	0. 2231

Table 15, finally, is constructed to facilitate a comparison of the principal data. Where no values for specific resistances were in hand, the measurements not being feasible, we supplied them by interpolations from our earlier papers on steel. Such values are distinguished by parentheses. The table will be readily intelligible.

TABLE 15.—*General digest. Mean results.*

Nos.	Temper.	s_0	Δ_0	v_0
I. $l=5.3$; $2\rho=1.9$	Commercial soft	(15)	7.8372	0.12760
	Glass hard	(44)	7.8092	0.12805
	Annealed, 100°, 1^{h}	(39)	7.8088	0.12806
	Annealed, 100°, 4^{h}	(37)	7.8094	0.12805
	Annealed, 100°, 8^{h}	(36)	7.8108	0.12803
	Annealed, 100°, 12^{h}	(36)	7.8114	0.12802
	Annealed, 200°, 30^{m}	(28)	7.8096	0.12805
	Annealed, 330°, 5^{m}	(21)	7.8236	0.12782
	Annealed, 620°, 5^{m}	(18)	7.8342	0.12765
	Annealed, 805°, 30^{m}	(17)	7.8361	0.12762
	Annealed (1,300°)	(19)	7.8465	0.12744
II. $l=10.11$; $2\rho=0.576$	Commercial soft	(15)	7.7033	0.12981
	Glass hard	(44)	7.6200	0.13123
	Annealed, 190°, 4^{m}	(32)	7.6542	0.13065
	Annealed, 330°, 2^{m}	(21)	7.6661	0.13044
	Annealed, 645°	(18)	7.7008	0.12986
	Annealed, 830°	(18)	7.7170	0.12958
	Annealed (1,300°)	(19)	7.7392	0.12922
55 to 60; 61 to 63. 21 pieces. $2\rho=0.127$.	Commercial soft	15.25	7.7337	0.12961
	Glass hard	43.29	7.6688	0.13040
	Annealed, 100°, 9^{h}	35.61	7.6976	0.12991
	Annealed, 200°, 2^{m}	33.11	7.6981	0.12990
	Annealed, 200°, 30^{m}	28.76	7.7030	0.12982
	Annealed, 330°, 30^{m}	20.61	7.7215	0.12951
	Annealed, 810°, 30^{m}	18.10	7.7872	0.12842
	Annealed (1,000°)	19.74	7.7865	0.12843
	Annealed (1,300°)	19.29	7.8007	0.12819
0. 18 pieces. $2\rho=0.226$	Commercial soft	(15)	7.81	0.1280
	Glass hard	(44)	7.6817	0.13018
	Annealed, 100°, 10^{m}	(42)	7.6943	0.12997
	Annealed, 100°, 7^{h}	(37)	7.7102	0.12970
	Annealed, 190°, 15^{m}	(31)	7.7251	0.12945
	Annealed, 330°, 8^{m}	(21)	7.7441	0.12913
	Annealed, 460°, 1^{h}	18.27	7.7641	0.12880
	Annealed, 720°	17.13	7.7793	0.12854
	Annealed (900°)	18.10	7.7840	0.12846
	Annealed (1,100°)	18.60	7.7865	0.12843
	Annealed (1,300°)	18.30	7.7856	0.12801
30 to 36; 21 to 29. $2\rho=0.081$. 72 pieces.	Commercial soft	16.27	7.7268	0.12942
	Glass hard	43.86	7.6547	0.13064
	Annealed, 100°, 1^{h}	39.26	7.6666	0.13044
	Annealed, 100°, 13^{h}	35.51	7.6745	0.13030
	Annealed, 190°, 4^{m}	30.82	7.6841	0.13014
	Annealed, 190°, 3^{h} 30^{m}	27.10	7.6808	0.13020
71 pieces	Do	27.10	7.6748	0.13030
	Annealed, 330°, 10^{m}	20.68	7.6806	0.13020
	Annealed, 470°	18.36	7.7190	0.12955
	Annealed, 530°	18.17	7.7227	0.12949
	Annealed, 690°	17.24	7.7272	0.12941
	Annealed, 810°	17.56	7.7586	0.12889
	Annealed, 1,000°	18.59	7.7705	0.12869
	Annealed, 1,100°			

In certain cases in the above tables it was necessary to interpolate values for the temperature at which wires are annealed, from the known power of the furnace used under given circumstances. All such values have been inclosed in parentheses.

The retrograde movement of density, observed when the rod No. I (see Table 5), thoroughly annealed at 100°, is further annealed at 200°, would seem to indicate the occurrence of shrinkage during the intervening lapse of 2½ years.

Graphic representation.—The results of the above tables are again perspicuously summarized in the graphic comparison, Fig. 1. We remark that the commercial state is distinguished in the diagram by a small *c* attached to the point, and it is to be borne in mind that only in the cases of wires Nos. 21 to 29 and Nos. 61 to 63 were the resistances for this state measured. In the three remaining cases we were obliged to interpolate a value, which was purposely chosen small. Density was always measured.

A few details relative to the figure are here in order. In view of the small variation of density of No. I, we are justified in anticipating a similarly small increment of resistance. It is known that the shortage in such a case is deducted from the variation of the glass-hard state. Hence the five hardest points are so nearly coincident in regard to resistance that the small increment of density in the glass-hard region is quite normal. The points have been spread out laterally in the diagram in order consistently to preserve the method of construction.

While operating with rods Nos. 21 to 29 we were so unfortunate as accidentally to lose one of the 72 pieces (see Table 11). The nature of the variation sought is thus exhibited in two independent phases. Nevertheless we believed ourselves justified in connecting the part of the locus obtained with 72 pieces with the part obtained with 71 pieces directly. The low value (marked *b* in the diagram) for the first of the latter points (annealed 190°, $3^h\ 30^m$) we discard, since insufficient care seems to have been taken in scouring and drying the 71 pieces over again. The difference of mean values for density at this stage of annealing is therefore attributable to an error in the weight for the low value.

DISCUSSION.

Immediate inferences.—If we regard these results as a whole, our first inference is that between the density and the electrical constants of steel there is no immediate connection whatever. Particularly in the case of thin wires, the initially enormous electrical variations correspond to comparatively small changes of density, whereas the latter become marked and striking when the former have nearly subsided. We may divide the whole series of phenomena into two parts or phases: the first part to include those variations which occur between "hard" and "annealed at 350°;" the second part to include the variations between

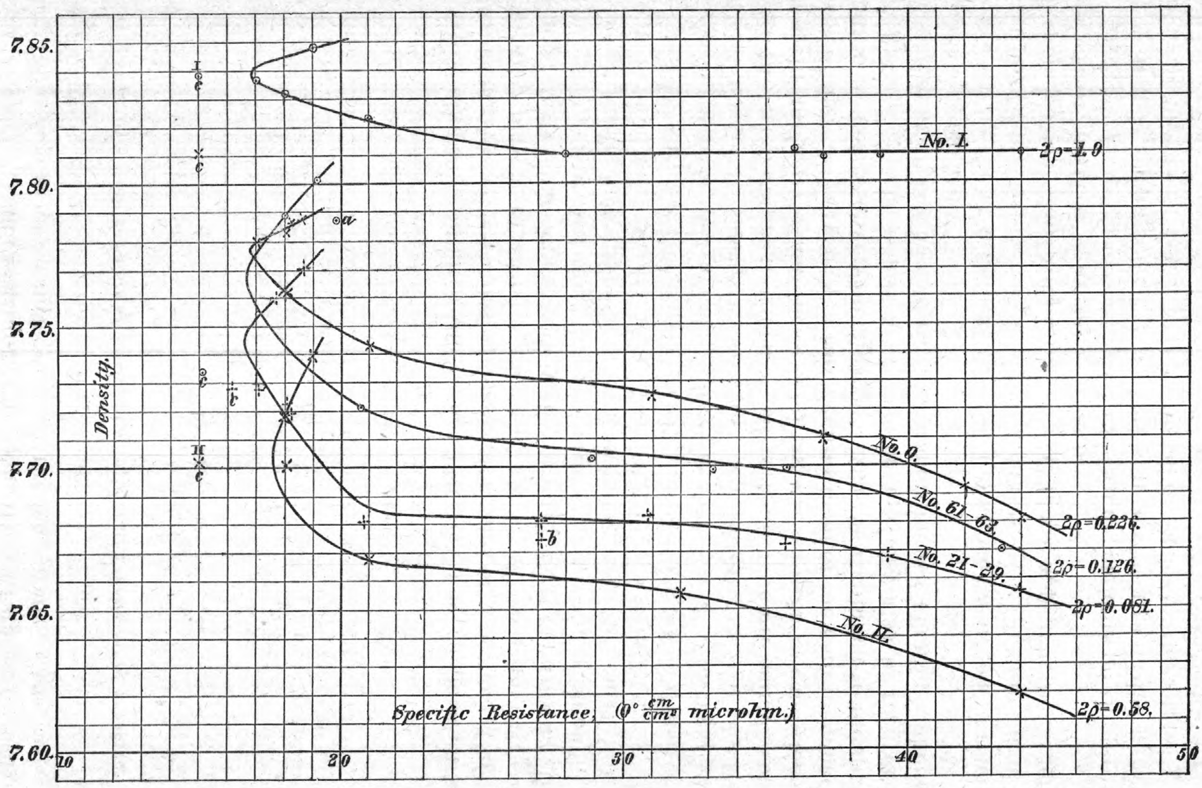

FIG. 1.—Diagram of the relation between the specific electrical resistance and the density of steel in different states of temper.

"350°" and "annealed at white heat." In Table 16 we denote by Δ_s, Δ_{350}, Δ_h, the densities; by s_s, s_{350}, s_h, the resistances corresponding to the "soft," the "annealed at 350°" and the "hard" states, respectively; by Δ_c, s_c, the density and resistance for the commercial states, respectively. The table then gives a concise view of the magnitude of the variations in question.

TABLE 16.—*Relative values of increment of volume and increment of resistance.*

	$-\frac{\Delta_h-\Delta_s}{\Delta_c}$	$-\frac{\Delta_h-\Delta_{350}}{\Delta_c}$	$-\frac{\Delta_{350}-\Delta_s}{\Delta_c}$	$\frac{s_h-s_{350}}{s_c}$	$\frac{s_{350}-s_c}{s_c}$
I	0.0048	0.0018	0.0029	....	....
II	0.0155	0.0060	0.0095	....	....
61 to 63	171	68	103	(1.51)	(0.35)
0	133	80	053	1.53	0.40
21 to 29	150	33	116	1.55	0.29
Mean	0.0131	0.0052	0.0079	....	....

This table substantiates the remarks made. The commercial state has been assumed as a datum simply for want of a better. Commercial wires may be regarded as annealed soft by slow cooling from high temperatures; but unfortunately they always carry a "drawn" strain. The results show that their density is by no means the maximum.

From the table we conclude that as we approach and enter into the region of red heat the density increases at an accelerated rate. It is a plausible surmise which associates this marked change of density with the occurrence of the Cumming-Gore[1] phenomenon of sudden expansion at red heat. Furthermore, we know and readily call to mind here that the temperature to which a rod is heated before sudden cooling and the intensity of hardness resulting are subject to conditions not unlike this. Finally, it is in the neighborhood of the said phenomenon that a marked reconversion of carbon from the combined to the uncombined form is to be looked for. This change may also be regarded as occurring at an accelerated rate, in proportion as Cumming's phenomenon is approached.

Regarding the results from this standpoint, we are urged to refer the first phase, just defined, to mechanical causes. On the other hand, the phenomena comprised within the second phase appear to be largely, if not wholly, induced by chemical causes.

Analysis of the phenomenon.—Of the two dependents on the physical state of steel, density and electrical resistance, the latter is distinguished from the former as being essentially conditioned by the intensity and the kind of strain which the steel rod carries. We may readily conceive a series of rods of like density, but which nevertheless have been strained in thoroughly different ways. The first phase of the above

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[1] Gore: Proc. Roy. Soc., XVII, 260, 1869.

phenomena (annealing between 0° and 350°) is thus elucidated, for we may imagine that within this interval the enormous glass-hard strain gradually subsides. The second phase of the phenomena, however, remains obscure; it is hard to see why so large a change of density is unaccompanied by a corresponding resistance-effect. We may remark, in passing, that the accepted electrical scale is partial to higher degrees of hardness; it blends and crowds the lower degrees. We would probably obtain a better distributer by using the logarithms of resistance constants instead of the mere numbers.

The way in which high temperatures act is, therefore, as yet quite obscure. We have failed clearly to discern the laws of such action. There will obviously coexist a number of secondary phenomena, so that the actual result obtained must be regarded as an aggregate of many superimposed effects. It is not remarkable, therefore, that our results fail to corroborate those of Dr. Fromme; that they are here quite at variance with his data; that we were unable to reproduce or to find his maximum density; that our process of annealing did not even force the resistance of the rod back to the small value for the commercial state.

We shall endeavor to enumerate the individual effects which together influence a rod exposed to high temperatures. The more important are: (1) Effect of kind of steel; (2) effect of repeated annealing; (3) effect of long continued heating; (4) effect of oxidation (decarburation); (5) effect of a change in the form or quality of carburation; (6) effect of the rate of cooling.

Among these the first may be dismissed. The different kinds of steel examined show the same behavior. We do not believe that the difference between Dr. Fromme's results and ours is to be ascribed to such a cause. The second point, the effect of repeated heating to a given high temperature, seems to be equally impotent, though we were not at first inclined to regard it so. Wires Nos. 21 to 29 were heated twice to 500°, approximately, without showing any marked difference in density or in electrical state. Long-continued heating, the third point, is known to produce pronounced changes in the degree and quality of carburation of cast iron; but, where the times of exposure amount to only one or two hours and where the quantity of carbon is small, the third effect may also be disregarded. The next point, however, relative to the effect of oxidation (decarburation) in changing the chemical composition of the rod, may be of very serious moment. We have stated that in our principal data no error due to oxidation is to be apprehended. It is improbable, moreover, that carbon should have been transferred by diffusion to the envelope of copper or platinum foil in any appreciable degree, or that gases of any kind should have passed through this envelope to the steel. The inner layers of the copper foil remained bright, although the outer layers were heavily oxidized. In some cases of very high temperature the platinum foil was observed to be dulled or stained where it had been in contact with the steel. Under these circumstances the rods were scoured with unusual care. Indeed, in all cases of possible contamination or corrosion, a sufficient thickness of external layer was removed. This the results for μ clearly show. In our original experiments, however, in which wires of very low resistance were obtained by the well-known methods of softening, the wires after being treated were invariably oxidized to corrosion. If now we remember that the resistance of a rod is largely dependent on its superficial layers, it is obvious, since decarburation causes the rod to approach nearer iron, that the variation of resistance to be anticipated has the sense of the effect actually observed. The importance of the fifth point, passage of carbon from combined to uncombined, we have no means of estimating. It may be the fundamental cause of the whole series of observed phenomena, and again its effect may be negligible.

To the last of the given points, the effect of the rate of cooling from the high temperature, we are inclined to attach paramount importance. In all the current processes for softening the condition of slow cooling seems to enter essentially. Rods Nos. 61 to 63 were heated to 1,000°, then cooled quickly (but not suddenly). The effect is marked, as is shown by the position of the point *a* in the diagram. The increment of resistance is especially large, and is the same in kind as that produced by sudden cooling. It would appear that to cool a wire in such a way as to leave it quite free from strains of any kind the operation must be conducted with exceeding slowness. Similiar liability to the retention of strains is observed in glass. Our wires were heated in gas-furnaces. The cooling may here be considered complete within two or three hours after the gas is shut off. Chwolson actually heated and cooled his wires in air. It may be plausibly argued, therefore, that the observed minimum of resistance is a secondary phenomenon, and that it is due to the appearance of strain in consequence of comparatively rapid cooling. Thus it becomes plain that the path of the second phase of the above phenomena is subject to pronounced variation, according as the rate at which cooling takes place is either large or small.

Density on the other hand seems to be much less sensitive as regards the rate of cooling. It is possible that with prolonged heating and very prolonged cooling Fromme's maximum may appear. In rods Nos. 0, after annealing at 1,300°, there is an apparent tendency in this direction, but it is so small as to be negligible. So far as the above researches go, the inference is far more probable that, barring effects of decarburation, the density of steel will be greater according as the operation of softening (ausglühen) is more and more carefully conducted; moreover, that for very prolonged cooling the minimum resistance will probably lose its character altogether.

Effect of structure.—Having endeavored to refer the observed relations between density and resistance, in part at least, to effects of stress, we desire finally to call to mind that, even in the case of the simplest elementary relation between these quantities, the aggregate result, when the rods examined are structurally heterogeneous, must necessarily be complex. We remark in passing that it seems to us too early to dismiss the relevant result derived in Bulletin No. 14, viz, the increments of resistance corresponding to a given increment of volume, whether the latter be produced by temper or by temperature, are of the same order. We contend that it is highly improbable that this result should be a mere chance coincidence.[1]

Given a hard rod consisting of p, coaxial, homogeneous, cylindrical shells. Let the right sections, the specific resistances, the specific volumes of these be

$$\begin{array}{l} q_1,\ q_2,\ q_3,\ \ldots\ldots\ q_p, \\ \quad s_1,\ s_2,\ s_3,\ \ldots\ldots\ s_p, \\ \quad\quad v_1,\ v_2,\ v_3,\ \ldots\ldots\ v_p, \end{array}$$

respectively. Let Q, S, V be the right section, the specific resistance, the specific volume, respectively, of the rod as a whole.

Suppose we assume that for an elementary homogeneous layer the simple relation which holds approximately for thermal expansion, obtains, viz,

$$s = nv + m \quad \ldots\ldots\ldots\ldots \quad (1)$$

Then, in consequence of (1),

$$S = \frac{Q}{\dfrac{q_1}{nv_1 + m} + \dfrac{q_2}{nv_2 + m} + \ldots\ldots} \quad \ldots\ldots \quad (2)$$

$$V = \frac{Q}{\dfrac{q_1}{v_1} + \dfrac{q_2}{v_2} + \ldots\ldots} \quad \ldots\ldots \quad (3)$$

equations incompatible with

$$S = nV + m$$

except under simple and inadmissible conditions. We advert in this connection to the fact that the observed relation between specific re-

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[1] Experiments on the internal structure of tempered steel (now in hand in some number and to be detailed in Bulletin 35, in press) lead to an incidental result which is of importance here. It appears that the immediate effect of decarburation is an increase of the density of the parts decarburized. This agrees with the anomalously large and striking results for the density of low-carbon steel, quite recently discussed by Mr. Miller and Mr. Kent (A. I. M. E., Halifax Meeting, 1885). If at high temperatures carbon may be withdrawn from steel by diffusion without perceptible surface oxidation, it is possible that the importance of the density-effect of decarburation has been underestimated in the text.— March, 1886.

sistance and thermo-electric power is *independent* of the structure of the tempered bar. Hence the facility with which its true form is investigated.

A clear interpretation of the phenomena discussed in this paper will only be possible, therefore, when a series of subsidiary experiments has supplied satisfactory results for the internal structure of tempered steel. Experiments to this end are in progress. The important bearing of the density-relations on problems connected with the maximum of magnetization will be discussed in a subsequent paper.

WASHINGTON—PRAGUE, *September* 9, 1885.

THE RELATION BETWEEN TIME OF EXPOSURE, TEMPER-VALUE, AND COLOR IN OXIDE FILMS ON STEEL.

By C. Barus and V. Strouhal.

VIEWS REGARDING THE FORMATION OF OXIDE COATS.

The phenomenon.—If a bright steel surface be heated in air to a temperature lying between 200° and 300° it will soon be covered with a film of oxide. The color, and hence we infer the thickness, of this film depends primarily upon the temperature of exposure, and a scale like the following is usually found in technical and metallurgical treatises on the subject:

Very pale yellow	220°
Straw yellow	240°
Brown yellow	260°
Light purple	280°
Dark purple	290°
Clear blue	300°
Pale blue	320°
Blue, tinged with green	330°

It is known, moreover, that the temper of hard steel subjected to the operation of annealing is similarly conditioned. Hence the oxide colors furnish the engineer a datum for the hardness of steel, of great practical utility and importance.

If we endeavor to analyze the physics of this simple and well-known phenomenon of oxidation, we unexpectedly encounter a problem of considerable interest. How are we to explain the fact that after the bright polished surface is jacketed with a protecting film of just finite thickness — a film, moreover, which, from its extreme thinness, we must regard continuous, elastic, tenacious, like scales of glass blown so thin as to be iridescent — further oxidation does not altogether cease? In other words, what is the process by which oxygen passes through the film; or, having decided upon a hypothesis, in how far can we prove it to be compatible with all the observed phenomenon, and in how far are the latter deducible from it?

Cause of oxidation.—With regard to a continuous film, the following consideration is clear at the outset: The outer surface of the film must be and remain oxidized as highly as is possible in air; the inner surface, continually in contact with iron, must be and remain reduced as far as is possible. In other words, if we measure unit of area along the surface of the film, and consider the quantity of oxygen contained in a cylinder with the said unit as a base and an axis normal to the surface of the film, then will the *limit* of the ratio of quantity of oxygen to height of cylinder, when height decreases indefinitely, be a *maximum* near the surface of film in contact with air and a *minimum* for the surface in contact with iron. It is presumable that between these limits the coefficient in question varies continuously. We have in mind, therefore, something very similar to the cause of flow in the mathematical theory of heat — the thermal gradient — and even more similar to the concentration-gradient in the theory of diffusion. In short, the distribution of the degree of oxidation along a normal to the layer is such as to be equivalent to a moving force in virtue of which oxygen is forced through the layer from its external surface to its internal surface. We therefore endeavor to regard the present phenomenon of oxidation as a kind of diffusion.

It is obvious that, with the object of further developing these views, we may enumerate the oxides of iron[1] and then make use either of a hypothesis like that proposed by Grotthus for electrolytic conduction; or, better, a hypothesis based upon the thermal activity of the oxidized molecules. But it is unnecessary to attempt this extension here.

Anticipative electrolytic effect.—A film possessing the properties specified has the essential qualities of an electrolyte. If we suppose one end of a strip of platinum foil or of platinum wire to be in contact with the outer layer of the film, while the other end is in continuous metallic contact (soldered) with the iron or steel, we have all the conditions involved in a galvanic circuit, in which the current passes from iron across the film to the platinum and thence back again to the iron. The electrolyte here is solid; but the possibility of solid electrolytes is by no means unexemplified — indeed, has of late elicited much experimental attention.[2] The efficiency of such an electrolyte is essentially dependent on temperature and on time of action, in a way which we shall presently endeavor to elucidate.

Under circumstances like those in question, electro-motive forces of relatively large intensity have indeed been observed and discussed by Franz,[3] Gaugain,[4] Jenkin,[5] and others. To our knowledge, however, they have invariably been explained as purely *thermo-electric* phenomena, in which the oxide film, kept at a different temperature at its outer

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[1] On the composition of different parts of the film in question, see Roscoe and Schorlemmer's Chemistry, II (2), p. 86. Appleton & Co., New York, 1884.

[2] Bidwell: Nature, XXXII, pp. 345, 391, 1885; Thompson: Nature, XXXII, p. 366, 1885.

[3] Franz: Pogg. Ann., LXXXV, p. 388, 1852.

[4] Gaugain: Comptes-Rend., XXXVI, pp. 612–616, 1853.

[5] Jenkin: Rep. Br. Assoc., 1861, (2), p. 34.

and inner surfaces, is the main source of the comparatively large electric effect. The possibility of thermo-currents under these circumstances is indisputable; the possibility of voltaic currents equally so. We apprehend that to separate the one class of currents distinctly from the other is a problem eliciting considerable experimental skill.[1]

Consequences of the theory.—The immediate consequences of the (diffusion) theory assumed are these: The rate at which oxidation takes place is greater as the film is thin; for, since the difference in oxidation of the anterior and posterior faces of the film is constant in value, it follows that the force tending to move oxygen across any interface is smaller in proportion as the film itself is thicker. In consequence of the solid medium, oxidation must cease entirely after a certain definite and limiting depth, dependent on temperature only, has been reached; that the depth and degree of oxidation (time $=\infty$) must increase with temperature, because temperature increases the thermal activity of the oxidized molecules of the film. Indeed, we may here seek to find a crucial difference between solids and liquids, inasmuch as in the former diffusion demonstrably ceases after a certain small thickness is permeated, whereas in liquids, as a result of vastly greater thermal mobility, diffusion is independent of thickness.

Within certain limits, therefore, an oxide film of given color can be obtained in an indefinite number of ways: at comparatively low temperatures, by long intervals of exposure; at relatively high temperatures, by short exposures. Curiously enough, the conditions subject to which a given oxide color appears are strikingly analogous to the conditions subject to which a given degree of temper is imparted to hard steel. It is possible, therefore, that the oxide film may be a criterion for the temper of a rod, *cœteris paribus*, of far greater critical sensitiveness than has hitherto been supposed; though it must first be investigated in what degree and upon what conditions, at a given temperature, the rate and nature of the variation of temper and the rate and nature of the color variation of the oxide film are convertible.

EXPERIMENTAL RESULTS.

Method of experiment.—The experiment which we finally decided upon is of the simplest kind, and yet it is capable of yielding a much larger return than we have thus far derived from it. Indeed, we believe that the method pursued will satisfactorily and crucially answer all the questions involved in the present discussion, except, of course, those referring to electrical currents.

A rectangular parallelopipedon or shaft of iron, 25 cm. high, 5 cm. broad, 5 cm. thick, is placed on a suitable tripod, with its faces vertical. The flame of a chimneyed Bunsen burner impinges against its base. To protect the sides, both from the flame and from direct radiation, a large,

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[1] A few experiments which we made here show the effect in question, but are otherwise not easily explained quantitatively.

thick, horizontal screen of asbestus board is adjusted, about 1 cm. above the bottom of the block. The upper 24 cm. are thus heated by conduction only.

This prism or block of iron was purposely chosen massive, *i. e.*, of large section, so that the diminution of temperature from the bottom upward would occur at a small uniform rate throughout. The colors are then ultimately distributed in wide bands. Experiments subsequently showed that the length might have been advantageously chosen two to three times that of the block selected. Insufficient attention (as we also found subsequently) was bestowed upon having the block scrupulously clean before the experiment was commenced; for in the colored surface finger-prints, for instance, could be distinctly discerned, the color at such spots always preceding, in degree, that of the untarnished surface of the bar. Thus the color bands, after long annealing, are liable to become distorted, oblique, and ill-defined. It is then difficult to obtain satisfactory measurements.

We may remark here that in using this block for obtaining the temper value of an oxide color two methods suggest themselves:

(1) We may produce a satisfactory succession of colors on the surface of the iron block by heating one end as described; provide these with an arbitrary fixed scale, something like Bunsen and Kirchhoff's spectroscopic scale; refer the color of hard steel wires annealed by exposure to air of known temperature during known time to the datum on this scale; finally, compare this value with the thermo-electric hardness of the wire, measured directly.

(2) Or we may drill into the bar narrow vertical holes closed at the lower end but extending to within a few millimeters of the base. Into these introduce the hard steel wire; compare the color bands between given isothermals on the surface of the block with the resistances of the parts of the steel rod comprehended between the same isothermals, respectively, by the aid of a Matthiessen-Hockin rider of 1 cm. length. The block is of course not to be heated until the steel wires are introduced. Both methods are in progress.

After the thermal flow has become stationary, temperature is distributed along the axis of the block in accordance with the well-known relation $t_1 + t_3 \mid t_2$, = const., where t_1, t_2, t_3 are the temperatures of any three consecutive equidistant points. Three measurements, therefore, enable us to interpolate the thermal state for any point of the block. Our values for temperature are determined thermo-electrically by aid of a couple of platinum and platinum-iridium alloy of known constants. The junction of this was hammered flat. During the exploration a brass clamp, one end of which was covered with asbestos felting, held the flat junction firmly against the part of the block to be examined.

Results.—In the Tables 1 to 5 which accompany the following protocol, e_{20} denotes the electromotive force (micro-volts) observed when the temperature of the cold junction of the thermo-couple is 20° C.; T is the corresponding temperature of the hot junction; *d* refers to the position or depth (cm.) of the adjoining temperature below the top of the block as a datum. Sometimes, to show the constancy of the distribution, the *times* at which the observations were respectively made are also annotated. Throughout the experiment the bottom of the block remains dark at a temperature of about 400°.

Tuesday, May 26, 1885 — 0 hour.

Experiment commenced. Flame ignited at 10^{h} a. m. Clear blue zone, 25 cm. *deep*, i. e., 25 cm. below the top plane of block.

12 hours.

Clear blue zone, 22 cm. deep. Top not observably colored.

Wednesday, May 27, 1885 — 24 hours.

Clear blue zone, 18 cm. deep. Top, straw yellow. The surface is mottled. Rough places, cracks, edges, color blue long before the surface is perceptibly colored at all. Finger-prints especially apparent.

36 hours.

Clear blue zone, 15 cm. deep. Top, yellow-brown.

TABLE 1.—*Distribution of temperature after* 36^{h}.

Elem. No.	e_{20}	*T*	*d*	*Time.*	Remarks.
		°		h m	
36..........	1,461	190	1	6 20	
	1,461	190	1	26	
	2,400	288	23	6 36	
	2,428	288	23	45	
	1,705	215	12	7 00	
	1,705	215	12	10	
	1,382	185	1	....	Clamp removed; element in mere contact with shaft.
	1,486	193	1	7 15	Clamp again adjusted.
	1,482	192	1	40	
	1,481	192	1	55	

Thursday, May 28, 1885 — 48 hours.

Clear blue zone, 14 cm. deep. Top, dark yellow-brown.

TABLE 2.—*Distribution of temperature after* 48^{h}.

Elem. No.	e_{20}	*T*	*d*
		°	
36........	1,346	175	1

No visible effect during the intervening 12^{h}, except a widening of the bands. Blue spots near the top, in rough places.

Friday, May 29, 1885—72 hours.

Clear blue zone, 13 cm. deep. Top, brown-purple.

TABLE 3.—*Distribution of temperature after* 72^h.

Elem. No.	e_{20}	T	d	Remarks.
		°		
36...............	1,453	189	0	Brown-purple.
	1,666	214	11	Blue.
	2,285	275	22	Steel-gray.
	1,758	224	....	Light blue lower boundary = maximum clear blue.

Bands too jagged for clear definition. Whole upper part of shaft dark brown to light purple, with spots and patches of blue. Cracks and rugosities purple-blue throughout.

Saturday, May 30, 1885—96 hours.

Clear blue zone, — cm. deep. Top, brown-purple. About as yesterday. Blue zone darker and wider. The white or steel-gray part higher, say 13 cm. There are blue spots on the top of the shaft, but all demarcation confused, so that it is difficult to define accurately.

Sunday, May 31, 1885—120 hours.

Clear blue zone, — cm. deep. Top, brown-purple. About as yesterday. Blue zone a little higher. Spots somewhat darker.

Wednesday, June 3, 1885—192 hours.

Clear blue zone, 10 cm. deep, Top, brown-purple. Rugosities, edges, cracks, spots, blue. Upper shaft brown purple.

Saturday, June 6, 1885—264 hours.

Clear blue zone, 8 cm. deep. Top, brown-purple, with lines of blue. Upper shaft brown-purple; spots of blue merging into steel-gray.

Tuesday, June 9, 1885—336 hours.

Clear blue zone, 9 cm. deep. Top, brown-purple. Color has visibly intensified, but is hard to define. Definite purple zone, between 9 cm. and 7 cm. deep, is the salient new feature.

Sunday, June 14, 1885—456 hours.

Clear blue zone, 8 cm. deep. Top, purple.

TABLE 4.—*Distribution of temperature after* 456^h.

Elem. No.	e_{20}	T	d	Remarks.
		°		
36............................	1,376	180	0	Light brown-purple.
	1,621	208	11	Blue.
	2,174	265	22	Black.

The whole upper shaft darker. From the bottom to 4 cm. upward (21 cm. deep), oxidized black, fading into steel-gray.

Tuesday, June 30, 1885 — 840 hours.

Clear blue zone, 8 cm. deep. Top, purple.

TABLE 5.—*Distribution of temperature after* 840^h.

Elem. No.	e_{20}	T	d	Remarks.
		°		
35	1, 342	175	1	
	1, 452	189	10	
	1, 865	233	20	
	1, 464	190	....	Mean blue zone.

Distribution of color..
- 0– 8 cm. deep..
  - Purple.
  - Blue.
  - Steel-gray.
- 10–20 cm. deep....Steel-gray, tinged with pink and green.
- 20–25 cm. deep....Shades very rapidly into black.

842 hours.

Gas shut off.

848 hours.

The block is just warm to the touch (35° C.), showing that in 5 hours after commencing the heating the thermal condition may be regarded practically stationary.

In Table 6 we give a digest of the different series of measurements for temperature-distribution, together with the mean results for the given interval of 840 hours. The latter are derived by graphic interpolation:

TABLE 6.—*Digest: Temperature* (*T*) *and depth* (*d*).

36 hours.		48 hours.		72 hours.		456 hours.		840 hours.		Mean results.	
T	d	T	d	T	d	T	d	T	d	T	d
°		°		°		°		°		°	
190	1	175	1	189	0	180	0	175	1	183	0
215	12	......	....	214	11	208	11	189	10	189	5
288	23	......	....	275	22	265	22	233	20	202	10
......	...	......	....	......	...	......	...	......	...	225	15
......	...	......	....	......	...	......	...	......	...	253	20
......	...	......	....	......	...	......	...	......	...	288	25

The mean results in this table agree as well with the direct measurements for clear blue, &c., as the conditions of measurement permit us to expect.

In Table 7, finally, the fundamental result of the above measurements is concisely summarized. The table contains the time of occurrence, position, and temperature of the blue film during the 840 hours of observation:

TABLE 7.—*Average temperature of the mean "clear blue" band, regarded as a function of time.*

Date.	Hours.	Depth.	Temperature.
			°
May 26, 1885	0	25	(300)
....	12	22	265
May 27, 1885	24	18	241
....	36	15	224
May 28, 1885	48	14	220
May 29, 1885	72	13	215
May 30, 1885	96	....	....
May 31, 1885	120	....	....
June 3, 1885	192	10	204
June 6, 1885	264	9	198
June 9, 1885	336	8	197
June 14, 1885	456	8	196
June 30, 1885	840	8	195

The final table is self-evident.

TABLE 8.—*Variation of color with time at* 185° (*top of brick*).

Time ..	0^h	12^h	24^h	36^h	48^h	72^h	300^h	800^h
Color ..	Colorless.	Not perceptibly colored.	Straw-yellow.	Yellow-brown.	Dark yellow-brown.	Brown-purple.	Purple..	Purple.

An inspection of Table 1 shows that during ordinary intervals of observation (12^h) the thermal distribution over the block may be regarded stationary. Within the very large interval 840 hours, however, fluctuations of temperature as large as 15° for points near the top and even 50° for points very near the base of the shaft are encountered. These are due to unavoidable fluctuations in the intensity of the flame. In taking the mean temperatures for the 35 days, the hurtful effects of these irregularities are satisfactorily eliminated.

Table 1, furthermore, shows the effect of measuring with and without the felted clamp, with a result equivalent to an excess of temperature of about 7° to 8° C. for the latter case. It is obvious that by protecting any point with a non-conducting envelope the temperature at this point soon rises above its normal (stationary temperature) value. Now, no illusory conclusions were to be apprehended for values of temperature too large, whereas values below the normal temperature at any given point would have led the observer into serious errors. We desired to investigate the lowest temperature at which the blue band, for instance, is producible. We saw no great objection to reporting the temperature a little higher than it actually was. It would, however, have been a fatal blow to some of our inferences had this temperature been erroneously measured too low.

Such errors and inaccuracies as have been introduced into the above protocol by distorted, oblique, and jagged bands, we shall in the future endeavor to eliminate by exposing well-polished and scrupulously clean surfaces only.

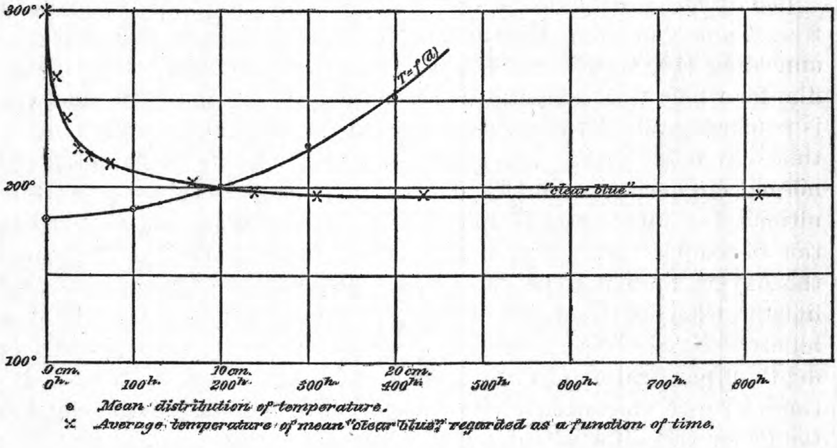
We add, in conclusion, that the original appearance of the shaft (say after 5 hours), with the blue only just emerged above the horizontal asbestus screen, and the final appearance (described under 840 hours in the protocol) are sufficiently in contrast to give pronounced emphasis to the results. We start with the upper shaft bright, the lower colored; we close with the upper shaft colored, the lower bright steel-gray.

DISCUSSION.

Difficulty of measurement.—Unless special optical apparatus be constructed, measurements which attempt to follow the change of position of a color among colors are always unsatisfactory, so far as the data are concerned. To the eye, however, the evidence furnished by such experiments is often strikingly conclusive. This is the case with the color diagram under discussion.

Color, temperature, time.—Our best mode of procedure will be that of first depicting graphically the mean positions of the given temperatures on the shaft, as contained in Table 6. Knowing these and the average depths of the blue band, its mean temperature at any given time follows at once. In Figure 2 we have constructed both the curves under consideration. The first shows a gradual ascent. It has been stated that it was for the purpose of securing this uniformity of slow increase of

Fig. 2.



temperature, and as a consequence wide color bands (blue zone 1 inch and more in width), that a block of large section was selected. Unfortunately the block ends abruptly with 185°, whereas it would have been desirable to terminate the shaft by not more than 50°. These desiderata are available to some extent, however, by lowering the flame or by inserting plates of metal or sheets of asbestus between flame and base of shaft.

The other curve shows exceedingly abrupt descent near the origin; but, as the rate decreases very rapidly, we find that after, say, 200 hours the horizontal asymptote is practically reached. The descent, however, continues at a very slow rate, and it is probably not quite complete even after 1,000 hours. Qualitatively this mode of variation must be very closely analogous to the change of temper actually observed on annealing hard steel. We could not, unfortunately, extend our experiments on the electrical effect of annealing beyond the small interval of about 12 hours of exposure; but from our results it is none the less conclusively deducible that the change of temper produced by annealing in 330° for only one minute is beyond the reach of 185° altogether, even though acting through infinite time. And this is precisely the interpretation of the "clear blue" color curve in Figure 2. Of course it is evident that, in the case of phenomena which owe their existence to and are evoked by causes wholly distinct, complete coincidence throughout their range of occurrence is as good as impossible. But the close resemblance of these two inherently dissimilar variations is the remarkable result which we desire to signalize here. Again, we would conjecture that high temperatures ($>200°$) are instantaneously efficient in contrast with low temperatures ($<200°$) where the effect is produced very gradually at a slowly decreasing rate. For final decision, however, it will be necessary to call further experimental data to our aid.

Conditions of oxidation.—Our second result, immediately deducible from Table 7 or from Figure 6, is this, that for each temperature of annealing (100°–500°) there exists a certain definite color of oxide film for which this temperature is characteristic; that this final color is reached gradually at a rate decreasing continually through infinite time. It follows that the depth to which superficial oxidation (the normal circumstances under discussion presupposed) can penetrate is ultimately a function of temperature only—but a sharply-defined function of temperature. For further elucidation we add that the size of the oxygen atom is to be estimated in fractions of millionths of a millimeter, whereas the depth or thickness of the color film is at least one hundred times the same unit. Hence we may estimate that the mean depth of penetration of an oxygen atom is expressible in thousands of times its own dimensions. We consider this general result relative to the (chemical) diffusion of a gas into a solid important, admitting, as it does, of quantitative discussion. Even if a certain constancy in the color effect of the action of a given temperature on steel has been assumed, this knowledge has been vague at best; its interpretation has been disregarded, and its true nature as a "limit" phenomenon—*i. e.*, the dependence of the temper value of any oxide tint on the temperature and the time of exposure—has, to our knowledge, been conjectured only in an incidental note of our own.[1]

Finally, the permeable depth increases rapidly with the temperature, until at incipient red heat the film is sufficiently thick to be brittle and liable to rupture, whereupon the present phenomenon, as such, ceases or is repeated in irregular succession.

Having endeavored to digest and interpret the experimental data in hand, we return therefore to the views expressed in the early paragraphs of this paper.

WASHINGTON—PRAGUE, *September* 15, 1885.

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[1] United States Geological Survey, Bulletin 14, p. 113, 1885.

MISCELLANEOUS ANALYSES.

MINERALS FROM WASHINGTON, D. C.

In an enlargement of the water supply of Washington, a rock tunnel, four miles long, with several vertical shafts tapping it from the surface, has been constructed. The minerals referred to below were collected at various points along the excavation by Mr. G. P. Merrill, of the United States National Museum, who will in due time publish a full account of them and of their modes of occurrence.

[A.—Saussurite from a gabbro found at the east shaft. Analysis by F. W. Clarke.]

Ignition	0.74
SiO_2	45.12
Al_2O_3	30.53
FeO	1.90
CaO	17.34
MgO	0.42
K_2O	1.09
Na_2O	2.02
	99.16

[B.—Hornblende from the same gabbro. Analysis by R. B. Riggs.]

H_2O	1.25
SiO_2	52.42
Al_2O_3	3.15
Fe_2O_3	3.60
FeO	8.36
MnO	0.11
CaO	14.33
MgO	15.85
K_2O	0.12
Na_2O	1.16
	100.35

[C.—Sphene; pale yellow, semi-translucent, imbedded in prochlorite. Sp. gr. 3.452. Analysis by F. W. Clarke.]

Ignition	0.54
SiO_2	30.10
TiO_2	40.82
CaO	28.08
MgO	0.40
MnO	Trace
	99.94

FAYALITE FROM THE YELLOWSTONE PARK.[1]

[Analysis by F. A. Gooch on only 0.24 gramme of material; 10.36 per cent. of material insoluble in HCl.]

SiO_2 in insoluble part	7.02
SiO_2 in soluble part	25.61
Fe_2O_3	14.92
FeO	51.75
Al_2O_3	Trace
MgO	1.66
CaO	None
Ignition	None
	100.96

SERPENTINE FROM NEWBURYPORT, MASS.

[Analysis by F. W. Clarke.]

H_2O	14.54
SiO_2	41.32
FeO	2.36
MgO	41.49
	99.71

KAOLIN FROM AIKEN, S. C.

[Analysis by F. W. Clarke.]

H_2O	14.10
Al_2O_3	40.25
SiO_2	45.56
	99.91

HORNBLENDE-ANDESITE FROM HAGUE VOLCANO, BOGUSLOFF ISLAND, BEHRING SEA, ALASKA.

Two samples collected by Lieut. G. M. Stoney and petrographically studied by Mr. G. P. Merrill.[2]

[A.—Rock described by Merrill as "consisting of a light-gray, slightly purplish, fine grained and porous groundmass, in which small glassy feldspars and dark brown and green hornblende-like crystals are readily distinguishable by the naked eye." A feldspar separated from it by Thoulet's method had a sp. gr. of 2.7 and contained 55.29 per cent. of silica, which is about the proportion for labradorite. Complete analysis by T. M. Chatard.]

Ignition	0.99
SiO_2	56.07
TiO_2	1.24
Al_2O_3	19.06
Fe_2O_3	5.39
FeO	0.92
MnO	0.23
CaO	7.70
MgO	2.12
P_2O_5	0.16
Na_2O	4.52
K_2O	1.24
	99.64

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[1] Fully described by J. P. Iddings, with crystallographic measurements by S. L. Penfield, in Am. Journ. Sci., July, 1885.

[2] Proc. U. S. Nat. Mus., Vol. VIII, No. 3, April 23, 1885.

[B.—A darker colored rock with a denser groundmass and carrying a larger proportion of microscopic hornblende and feldspar crystals. Analysis by T. M. Chatard.]

	1.	2.	*Mean.*
Ignition	0.34	0.34	0.34
SiO_2	51.46	51.63	51.54
TiO_2	0.32	......	0.32
Al_2O_3	20.26	20.35	20.31
Fe_2O_3	4.64	......	4.64
FeO	3.56	......	3.56
Mno	0.32	0.32	0.32
CaO	9.55	9.56	9.55
MgO	3.16	3.16	3.16
P_2O_5	0.57	......	0.57
K_2O	2.47	......	2.47
Na_2O	4.29	......	4.29
	100.94		101.07

FOUR ERUPTIVE ROCKS FROM NEW MEXICO.

[Collected by Capt. C. E. Dutton.]

[A.—Lava from a cañon on the east side of San Mateo Mountains. Analysis by T. M. Chatard.]

Ignition	0.52
SiO_2	68.40
Al_2O_3	17.99
Fe_2O_3	2.66
FeO	1.63
MnO	0.21
CaO	0.67
MgO	0.49
K_2O	3.54
Na_2O	4.54
	100.65

[B.—Rock from a cañon on the east side of San Mateo Mountains. Analysis by T. M. Chatard.]

Ignition	0.16
SiO_2	65.51
TiO_2	0.92
P_2O_5	0.07
Al_2O_3	16.89
Fe_2O_3	1.41
FeO	2.52
MnO	0.31
CaO	1.19
MgO	0.39
K_2O	5.02
Na_2O	6.42
	100.81

[C.—Rock from 6 miles northeast of Grant's. Analysis by T. M. Chatard.]

H_2O	1.38
$CO_2 = 5.77\ CaCO_3$	2.56
SiO_2	49.80
TiO_2	2.67
P_2O_5	0.73
Al_2O_3	15.33
FeO. No Fe_2O_3	7.44
MnO	0.30
CaO	7.19
MgO	6.61
K_2O	4.36
Na_2O	2.71
	101.08

[D.—Basalt from 6 miles northeast of Grant's. Analysis by T. M. Chatard.]

H_2O	0.36
SiO_2	47.54
TiO_2	2.76
P_2O_5	0.51
Al_2O_3	16.73
Fe_2O_3	6.69
FeO	6.67
MnO	0.19
BaO	0.03
CaO	8.74
MgO	6.38
Na_2O	2.81
K_2O	1.10
	100.51

An estimation of CO_2 gave 0.30 %; but a part of this was due to the permeability of the platinum tubulated crucible.

DACITE FROM WASHOE, NEVADA.[1]

[From spur northeast of McClellan Peak, near the American Flat Road. Analysis by F. A. Gooch.]

SiO_2	69.96
Al_2O_3	15.79
Fe_2O_3	2.50
CaO	1.73
MgO	0.64
Na_2O	3.80
K_2O	4.12
Ignition	1.53
	100.07

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[1] See Hague and Iddings, Bulletin No. 17, United States Geological Survey.

RHYOLITE FROM WASHOE, NEVADA.[1]

[Locality south-southeast of McClellan Peak. Analysis by F. A. Gooch.]

SiO_2	73.07
Al_2O_3	11.78
Fe_2O_3	2.30
CaO	2.02
MgO	0.39
Na_2O	1.19
K_2O	6.84
Ignition	2.24
	99.83

BLUE OHIO SANDSTONE.

[A building stone from quarries near Cleveland. Analysis by T. M. Chatard.]

SiO_2	91.67
Al_2O_3	6.92
Fe_2O_3	Trace
CaO	0.28
MgO	0.34
Ignition	1.17
	100.38

Insoluble in HCl, 97.50.

SANDSTONE FROM MICHIGAN.

[A yellow sandstone, quarried as a building stone at Stony Point. Analysis by F. W. Clarke.]

SiO_2	84.57
Fe_2O_3	6.48
Al_2O_3	5.90
MgO	0.68
Ignition	1.92
Alkalies	Undet.
	99.55

Insoluble in HCl, 91.87. The portion soluble in HCl contained 6.23 of the ferric oxide. The iron and magnesia are practically all in the cement, but the sand particles contain some silicate of aluminum.

TWO CLAYS FROM HENRY COUNTY, ILLINOIS.

[A.—On burning becomes reddish. Analysis by T. M. Chatard.]

H_2O	15.57
SiO_2	46.12
P_2O_5	0.08
TiO_2	0.79
Al_2O_3	15.24
Fe_2O_3	4.41
MnO	0.28
CaO	8.63
MgO	3.63
K_2O	3.79
Na_2O	1.54
	100.08

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[1] See Hague and Iddings, Bulletin No. 17, United States Geological Survey.

[B.—Burns reddish, but lighter than A. Analysis by T. M. Chatard.]

H_2O	18.64
SiO_2	42.58
P_2O_5	0.10
TiO_2	0.64
Al_2O_3	12.16
Fe_2O_3	3.90
MnO	0.09
CaO	11.33
MgO	4.32
K_2O	3.88
Na_2O	1.96
	99.60

FOUR RESIDUARY CLAYS FROM WISCONSIN.

Collected by Prof. T. C. Chamberlin. Analyses by R. B. Riggs. Material dried at 100°.

[A.—Clay from Dodgeville, 4½ feet below the surface, 4 feet above rock.]

SiO_2	71.13
Al_2O_3	12.50
Fe_2O_3	5.52
FeO	0.45
TiO_2	0.45
P_2O_5	0.02
MnO	0.04
CaO	0.85
MgO	0.38
Na_2O	2.19
K_2O	1.61
H_2O (includes H of organic matter)	4.63
CO_2	0.43
C (in organic matter)	0.19
	100.39

[B.—Same locality, 8½ feet below the surface, in contact with rock.]

SiO_2	49.59
Al_2O_3	18.64
Fe_2O_3	17.19
FeO	0.27
TiO_2	0.28
P_2O_5	0.03
MnO	0.01
CaO	0.93
MgO	0.73
Na_2O	0.80
K_2O	0.93
H_2O (includes organic H)	10.46
CO_2	0.30
C (organic)	0.34
	100.50

[C.—Clay from one mile west of Cobb, 3 feet below the surface, 1½ foot above rock.]

SiO_2	53.09
Al_2O_3	21.43
Fe_2O_3	8.53
FeO	0.86
TiO_2	0.16
P_2O_5	0.03
MnO	0.03
CaO	0.95
MgO	1.43
Na_2O	1.45
K_2O	0.83
H_2O (includes organic H)	10.79
CO_2	0.29
C (organic)	0.22
	100.09

[D.—Same locality as C, 4½ feet below the surface, in contact with rock.]

SiO_2	49.13
Al_2O_3	20.08
Fe_2O_3	11.04
FeO	0.93
TiO_2	0.13
P_2O_5	0.04
MnO	0.06
CaO	1.22
MgO	1.92
Na_2O	1.33
K_2O	1.60
H_2O (includes organic H)	11.72
CO_2	0.39
C (organic)	1.09
	100.68

MARITIME SOILS FROM MASSACHUSETTS.

Seven samples of salt-marsh soils collected by Professor N. S. Shaler. Partial analyses by R. B. Riggs.

[A.—Three soils from Green Harbor River, Marshfield: (1) Reclaimed salt-marsh. Average sample of soil from surface to two feet deep. Planted with onions. (2) Diked land. Average surface sample, second year of tillage. (3) Average sample of marine marsh immediately outside of dike.]

	1.	2.	3.
Carbon of organic matter	3.07	3.67	12.63
NaCl	0.36	0.15	6.70
Na_2O	2.43	2.19	2.33
K_2O	1.43	1.09	1.44
P_2O_5	0.17	Undet.	Undet.

[B.—Three soils from marine marsh, Charles River, Mt. Auburn street, Cambridge: (1) Lower portion of eel-grass layer; (2) Middle portion of eel-grass layer; (3) Middle portion of upper layer.]

	1.	2.	3.
Carbon of organic matter	3.83	4.22	12.68
NaCl	2.36	1.80	4.65
Na_2O	2.40	2.10	2.31
K_2O	1.76	1.80	1.89
P_2O_5	0.15	Undet.	0.07
CaO	Undet.	1.51	1.29

[C.—Soil from marine marsh, Mystic River, Malden. Average sample of a section from surface to three feet deep.]

Carbon of organic matter	3.06
NaCl	1.30
Na_2O	2.33
K_2O	1.70

OÖLITIC SAND FROM SHORE OF GREAT SALT LAKE.

Collected by I. C. Russell and analyzed by T. M. Chatard. The material consisted of small spheroidal grains, grayish-white in color, and with an admixture of a few dark particles. Washing with water extracted no sulphates and only traces of chlorides. After treatment with hydrochloric acid, a residue of grains of quartz, clay, and a little organic matter was left.

Insoluble in HCl	4.03
Organic matter	0.27
H_2O	0.83
Fe_2O_3 and Al_2O_3	0.20
CaO	51.33
MgO	0.72
Na_2O and K_2O	0.63
SO_3	0.89
P_2O_5	Trace
CO_2	41.07
	99.97

An impure calcium carbonate.

TWO INCRUSTATIONS FROM NEVADA.

Analyses by T. M. Chatard of the portions soluble in water.

A.—Grayish pulverulent crusts, from the surface of a playa, North Arm of *Old* Walker Lake. One gramme of material yields 0.2978 grm.

of soluble substance, or 29.78 per cent. The latter, analyzed as if it were an independent substance, gave the following results:

		Per cent. of total soluble.	Probable combination.	
By weight.				
SiO_2	0.0058	1.95	SiO_2	0.0058
K	0.0018	0.60	KCl	0.0035
Na	0.1159	38.92	NaCl	0.0075
Cl	0.0063	2.16	$Na_2B_4O_7$	0.0123
SO_4	0.0350	11.75	Na_2SO_4	0.0518
B_4O_7	0.0095	3.19	Na_2CO_3	0.2152
	0.1743			0.2961
CO_3 by difference	0.1235	41.43	99.43 % accounted for.	
	0.2978	100.00		

Or, to express the results in different form, the probable composition may be reckoned into percentages, as follows:

SiO_2	1.96
KCl	1.18
NaCl	2.53
$Na_2B_4O_7$	4.15
Na_2SO_4	17.49
Na_2CO_3	72.69
	100.00

B.—Incrustation from five miles west of Black Rock. One gramme of material gave 0.2310 grm., or 23.10 per cent., soluble in water. The latter, reckoned up to 100 per cent. and analyzed independently as under A, gave results as follows:

		Per cent. of total soluble.	Probable combination.		
By weight.			*By weight.*		*By percentage.*
SiO_2	0.0050	2.16	SiO_2	0.0050	2.18
K	0.0017	0.74	KCl	0.0032	1.39
Na	0.0832	36.02	NaCl	0.1362	59.32
Cl	0.0841	36.40	$Na_2B_4O_7$	0.0023	1.00
SO_4	0.0420	18.18	Na_2SO_4	0.0621	27.05
B_4O_7	0.0018	0.78	Na_2CO_3	0.0208	9.06
	0.2178			0.2296	100.00
CO_3, by difference	0.0132	5.72	99.43 % of the original 0.2310.		
	0.2310	100 00			

MARL FROM WA KEENEY, TREGO COUNTY, KANSAS.

[From a large deposit found near the surface. Analysis by F. W. Clarke.]

H_2O	1.77
CO_2	35.03
SiO_2	14.06
Fe_2O_3	5.10
MgO	0.50
CaO	43.05
	99.51

INCRUSTATION FROM CASING OF "GRAVEL-BAR GAS-WELL," KISKIMINITAS RIVER, ARMSTRONG COUNTY, PENNSYLVANIA.

[Partial analysis by E. Whitfield.]

Al_2O_3	41.10
SiO_2	50.70
H_2O	3.95
	95.75

Small quantities of iron, magnesia, and organic matter were not determined. The substance is interesting, on account of its mode of occurrence and from the fact that after deducting impurities its composition approximates very closely to the definite silicate, Al_2O_3, 2 SiO_2.

TWO PORCELAIN CLAYS FROM CHINA.

These clays were presented to the United States National Museum by Mr. Arthur B. French, of Boston, who obtained them in person at one of the Chinese potteries at King-te-Ching. They had been prepared for use before reaching the potteries, and were pressed into the form of bricks, each bearing in Chinese characters a stamped impression containing the name of the maker. On account of the absolute authenticity of the material it was thought that analyses might have special value for purposes of comparison with American clays. The sample marked A, of which only a few fragments were obtained, represents material used in the manufacture of the finest white porcelain. Sample B, which has a faint brownish or creamy tinge, was represented by nearly an entire brick, and is the material used in making the so-called "Blue Canton" ware.

[Analyses by E. Whitfield.]

A.

SiO_2	73.55
Al_2O_3	21.09
CaO	2.55
MgO	0.15
H_2O	2.62
	99.96

B.

SiO_2	73.55
Al_2O_3 (contains a little Fe_2O_3)	18.98
CaO	1.58
MgO	1.08
H_2O	1.96
SO_3	0.28
K_2O	0.46
Na_2O	2.09
	99.98

ANCIENT MEXICAN CEMENT.

[From an antique stone floor on the Hill of Texcocingo. Analysis by F. W. Clarke.]

H_2O	7.54
CO_2	18.87
SiO_2	35.56
Al_2O_3, with Fe_2O_3	10.34
CaO	25.41
MgO	2.79
	100.51

Insoluble in HCl, 38.25 per cent. Evidently an ordinary lime-sand cement.

BROWN IRON ORE FROM J. F. C. TALBOTT'S ORE BED, NEAR TIMONIUM, MD.

[Analysis by R. B. Riggs.]

Ignition	12.41
Fe	58.52
Mn	0.34
SiO_2	3.37
S	0.37
P	0.06
Oxygen for Fe and Mn	25.23
	100.30

BROWN IRON ORE FROM D. R. BAKER'S LAND, SHAVER'S MOUNTAIN, RANDOLPH COUNTY, WEST VIRGINIA.

[Analysis by E. Whitfield.]

Fe	47.530
P	0.138
S	0.298
SiO_2	18.930
MnO	0.203

BROWN IRON ORE FROM GOFF AND CRAWFORD'S LAND, ROARING CREEK DISTRICT, RANDOLPH COUNTY, WEST VIRGINIA.

[Analysis by E. Whitfield.]

Fe	39.210
P	0.157
S	0.169
SiO_2	32.790
MnO	0.350

BROWN IRON ORE FROM M'CURRENCE'S LAND, MILL CREEK, RANDOLPH COUNTY, WEST VIRGINIA.

[Analysis by E. Whitfield.]

Fe	44.270
P	0.251
S	0.155
SiO_2	25.400
MnO	0.075

COAL FROM HART'S BANK, RICH MOUNTAIN, RANDOLPH COUNTY, WEST VIRGINIA.

[Analysis by E. Whitfield.]

Water	1.29
Volatile hydrocarbons, &c	31.77
Fixed carbon	62.48
Ash	4.46
	100.00
Sulphur	0.54

Coke, good; ash, pink.

COAL FROM TALBOT'S BANK, ROARING CREEK DISTRICT, RANDOLPH COUNTY, WEST VIRGINIA.

[Analyses by E. Whitfield.]

[A, 3½-foot vein; B, 18-inch vein.]

	A.	B.
Water	0.84	1.14
Volatile hydrocarbons, &c	29.97	31.46
Fixed carbon	60.53	60.71
Ash	8.66	6.69
	100.00	100.00
Sulphur	0.98	1.02

Coke, good; ash, white.

COAL FROM W. H. WILSON'S BANK, NEAR HUTTONSVILLE, RANDOLPH COUNTY, WEST VIRGINIA.

[Analyses by E. Whitfield.]

[A, 13½-foot vein; B, 22-inch vein.]

	A.	B.
Water	0.63	0.77
Volatile hydrocarbons, &c	34.30	34.94
Fixed carbon	55.94	56.96
Ash	9.13	7.33
	100.00	100.00
Sulphur	0.81	1.55

Coke, good; ash, white.

COAL AND LIMESTONE FROM E. T. JONES'S LAND, SHAVER'S MOUNTAIN, RANDOLPH COUNTY, WEST VIRGINIA.

[Analyses by E. Whitfield.]

COAL.

Water	1.54
Volatile hydrocarbons, &c	24.48
Fixed carbon	70.13
Ash	3.85
	100.00
Sulphur	0.54

Coke, fair; ash, pink.

LIMESTONE.

Insoluble	19.87
Fe_2O_3 and Al_2O_3	4.09
CaO	41.29
MgO	.95
CO_2 and H_2O	34.27
	100.47

LIGNITE FROM THE TURTLE MOUNTAINS, DAKOTA.

[Analysis by E. Whitfield.]

Water	13.98
Volatile hydrocarbons	40.81
Fixed carbon	36.90
Ash	8.31
	100.00

COAL FROM ARIZONA.

[Collected by C. D. Walcott in Deer Creek Valley, 13 miles south of the San Carlos Indian Agency. Four samples. Analyses by E. Whitfield.]

	1.	2.	3.	4.
Water	1.59	0.48	3.27	0.56
Volatile hydrocarbons	15.79	19.81	12.51	17.50
Fixed carbon	49.72	61.01	5.72	60.85
Ash	32.90	18.70	78.50	21.09
	100.00	100.00	100.00	100.00

No. 3 was merely shale; Nos. 1 and 2 gave poor coke; No. 4, fair coke; ash, pink, except in No. 3.

WATER FROM MATTHEWS'S WARM SPRINGS, NEAR BOZEMAN, MONT.

[Analysis by R. B. Riggs.]

[Reported temperature of spring, 44°.5 C. Total solids, 0.5925 gramme to the liter.]

Found.		Per cent. of total solids.	Probable combination.	
SiO_2	0.1366	23.05	SiO_2	0.0826
SO_4	0.1335	22.53	Na_2SiO_3	0.1098
CO_3	0.0719	12.13	$CaCO_3$	0.0390
Cl	0.0505	8.52	$MgCO_3$	0.0036
Ca	0.0136	2.30	Na_2CO_3	0.0750
Mg	0.0010	0.16	KCl	0.0134
Na	0.1640	27.69	NaCl	0.0707
K	0.0070	1.18	Na_2SO_4	0.1974
	0.5781	97.56		0.5915
O in SiO_3	0.0134		99.83 per cent. accounted for.	
	0.5915			

The carbonic acid was determined directly. The SiO_3 was computed to satisfy the uncombined base left over after saturating all other acids.

WATER FROM WHITE SULPHUR SPRINGS, MEAGHER COUNTY, MONT.

[Analysis by R. E. Riggs.]

[The water of Spring No. 2 was taken. It contained traces of H_2S. Reported temperature, 45°.5 C. Total solids, 1.551 grammes to the liter.]

Found.		Per cent. of total solids.	Probable combination.	
SiO_2	0.0425	2.74	SiO_2	0.0330
SO_4	0.3025	19.50	Na_2SiO_3	0.0194
CO_3	0.4240	27.34	$CaCO_3$	0.1280
Cl	0.1875	12.09	$MgCO_3$	0.0438
Ca	0.0512	3.30	Na_2CO_3	0.5571
Mg	0.0125	0.79	Kcl	0.0807
K	0.0425	2.74	NaCl	0.2460
Na	0.4900	31.59	Na_2SO_4	0.4463
Li	Trace			1.5543
	1.5527	100.09	100.21 per cent. total.	
O in SiO_3	.0016			
	1.5543			

The SiO_3 was reckoned to saturate the uncombined base left over after satisfying all other acids.

WATER FROM MINERAL SPRING ONE MILE WEST OF SANTA FÉ, NEW MEXICO.

[Analysis by F. W. Clarke.]

[Total solids, 0.2800 gramme to the liter.]

Found.		Per cent. of total solids.	Probable combination.	
SiO_2	0.0220	7.85	SiO_2	0.0220
Ca	0.0634	22.67	$CaCO_3$	0.1538
Mg	0.0173	6.17	$MgCO_3$	0.0605
SO_4	0.0187	6.67	$CaSO_4$	0.0050
Cl	0.0117	4.18	NaCl	0.0193
Na	0.0149	5.32	Na_2SO_4	0.0225
	0.1480			0.2831
CO_3, by difference	0.1320	47.14	101.11 per cent. total.	
	0.2800	100.00		

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