

June 18, 1885.

THE PRESIDENT in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

Sir Andrew Clark, Bart., Dr. Francis R. Japp, Dr. Arthur Milnes Marshall, and Mr. William Mitchinson Hicks were admitted into the Society.

The following Papers were read:—

- I. "The Action of Tidal Streams on Metals during Diffusion of Salt and Fresh Water. Experimental Research. Part II (Gravimetric)." By THOMAS ANDREWS, F.R.S.E., Wortley Iron Works, near Sheffield. Communicated by Professor G. G. STOKES, Sec. R.S. Received May 29, 1885.

In a paper last session "On the Electromotive Force during Diffusion in Tidal Streams" (see "Proceedings Royal Society," No. 232), the author recorded the electrical part of this investigation. The present communication contains the concluding gravimetric experiments of the research. The effects attending the diffusion of the salt and fresh water in tidal estuaries, on parts of the same metal, were estimated in each case for a period of *one year*, during which the metals were constantly exposed to conditions of galvanic action similar to those obtaining in some tidal streams. The results demonstrate that electric disintegration of the nature alluded to in this and the former paper (*viz.*, the galvanic destructive action on parts of even the same metal, arising from difference of potential during diffusion between the surface and lower waters in a tidal stream) is, on comparison with other investigations by the author, apparently of much greater extent than the loss either from simple corrosion in sea water alone, or than that which ensues from the action on each other of dissimilar metals of this group (such as wrought iron, cast metals and steels) in galvanic connexion in sea water. The wrought iron, steels, and cast metals used were from the author's standard samples of known composition in the form of

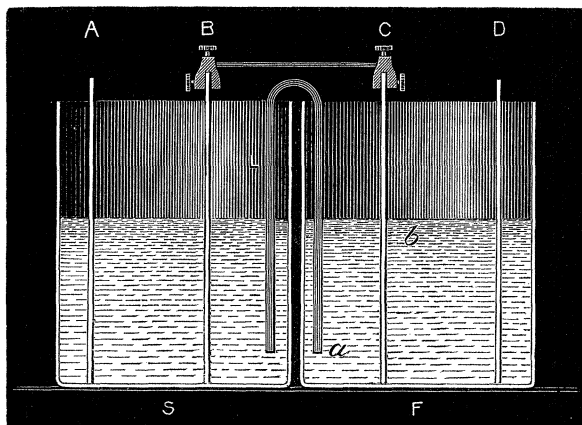
bright polished plates, of similar manufacture and general composition to the metals employed in the former paper.

Table A.—Analysis of the Wrought Iron, Steels, and Cast Metals employed.

Description.	Graphitic carbon.	Combined carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.	Iron (by difference).	Total.
Wrought iron .....	...	none	0·392	0·034	0·270	0·194	99·110	100·000
"Soft" Bessemer steel.....	...	0·150	0·015	0·111	0·064	0·540	99·120	100·000
"Soft" Siemens-Martin steel .....	...	0·170	0·071	0·117	0·077	0·627	98·938	100·000
"Soft" cast steel.....	...	0·460	0·074	0·025	0·210	0·184	99·047	100·000
"Hard" Bessemer steel.....	...	0·510	0·068	0·113	0·087	1·153	98·069	100·000
Best cast metal, No. 1 .....	2·780	0·390	2·340	0·090	0·580	0·450	93·370	100·000
Common cast metal, No. 2.....	2·620	0·670	1·940	0·090	0·950	0·520	93·210	100·000

The exposed part of each plate was 3 inches square by  $\frac{1}{8}$  inch thick. There was, however, a shank (3 inches long by  $\frac{1}{8}$  inch square) left in the centre of each plate for connecting purposes. The method of experimentation was as follows, see sketch, fig. 1: various interesting results were obtained by this arrangement of the cells.

FIG. 1.



Sketch of one set of the Diffusion Cells.

Four plates, A, B, C, and D (cut from one large plate of each of the metals, so that the four experimental plates of each set were practically of the same composition, molecular structure, &c.), were arranged as shown in fig. 1, each plate having been previously dried at 212° F., and weighed on the balance.

The plate A standing alone and unconnected was immersed in the vessel S containing a measured quantity of sea water.

The plate D also stood unconnected in the vessel F, and the action on this plate was similar to that on plate C, though somewhat modified in extent. This plate, although standing isolated, afforded another confirmatory indication of the extensive corrosion of metals exposed in water less saline at the surface than near the bottom, notwithstanding that the total salinity of the water in vessel F was greatly below that of the sea water.

The plate B was immersed in the sea water, but galvanically connected with the plate C in the vessel F.

In the case of the last two plates B and C, circuit was completed, and slow but continuous diffusion between the two solutions accomplished by means of a triple fold of soft moistened chamois-leather L (1 inch wide), one end of which was immersed deeply in the sea water, the other to an equal depth in the distilled water, see fig. 1. The sea water was obtained regularly from Filey Bay. The vessel was filled at the commencement with 25 fluid ounces of sea water, the vessel F with the same volume of distilled water. Both were emptied by siphon (without disturbing the plates) and each carefully refilled with their respective waters periodically every fourteen days for a total period of *fifty-two weeks*. Seven pairs of such diffusion cells of equal size were employed in the investigation. At the termination the plates were taken out, washed, carefully cleaned, dried at 212° F., and again weighed on the balance, and the corrosive effects determined by their relative loss in weight—the results are summarised in Table C.

The arrangement, fig. 1, was made so that the plate C, from its position, was exposed near the bottom at (*a*) to the action of water containing rather more salt than the water adjacent to the top at (*b*), whilst constant diffusion was at the same time proceeding, the salt water from vessel S also coming over into the distilled water at an increasing ratio, by means of the soft moist leather connexion; the water, however, about the position (*b*) nearer the surface, maintained a less saline composition than at (*a*), and the estimation of this difference between top and bottom water during the periodic slow diffusions, is shown in the following analysis, selected as an example from a number of similar observations taken at intervals during the progress of the investigation.

It will be seen that the diffusion cell arrangements allowed equilibrium of composition between bottom and surface to be restored in about fourteen days. As there was easy communication (about  $\frac{1}{2}$  inch) around the edges, not only of the plate C, but of the others, the fluid during diffusion in vessel F would probably arrange itself in layers of fairly equal density therein. These diffusion results also

compare favourably with statistics (examined and formerly referred to by the author, and some of which are given in the Appendix) as to differences of composition between surface and bottom waters during diffusion in some portions of such a tidal stream as the Thames, and therefore afford an approximation to effects arising from similar conditions existing during such tidal action; the proportional difference of salinity between top and bottom waters in parts of the Thames during certain states of tide, &c., being, however, sometimes greater than the experimental divergencies given on Table B.

Table B.—Analysis of Water from Diffusion Cell. Results in grains per Gallon.

Time from commencement of each diffusion.	Sodium chloride from position (a) near bottom.	Sodium chloride from position (b) near surface.	Difference of composition between water about (a) and (b)
1 day . . . . .	1·44	1·32	0·12
2 days . . . . .	2·87	2·64	0·23
3 " . . . . .	4·31	3·95	0·36
4 " . . . . .	5·90	5·01	0·89
5 " . . . . .	7·64	5·81	1·83
6 " . . . . .	9·38	6·61	2·77
7 " . . . . .	11·12	7·41	3·71
8 " . . . . .	22·19	19·42	2·77
9 " . . . . .	33·26	31·43	1·83
10 " . . . . .	44·32	43·44	0·88
11 " . . . . .	50·14	49·79	0·35
12 " . . . . .	50·73	50·49	0·24
13 " . . . . .	51·32	51·19	0·13
14 " . . . . .	51·90	51·90	Nil.

The samples of water for analysis were carefully taken from vessel F by pipette at points indicated on fig. 1 for convenience and accuracy, so as least sensibly to disturb the solution.

The electric action between the plate (which was the positive metal throughout the whole period) in the sea water and that in the other water, was in course of the research ascertained by occasionally introducing in the circuit a delicate galvanometer of known resistance and constants, and the resistance of the cells having been regularly determined, the highest E.M.F., in the case of two representative plates, was found to be about 0·14 volt, which gradually reduced as diffusion proceeded.

The loss by simple corrosion in the sea water alone, as compared with that taking place in the diffusing salt and fresh water, is shown by the relative behaviour of the two plates A and C, of the same

metal in each case, from which it is manifest that a diffusing mixture of salt and fresh water, although containing a comparatively small proportion of saline matter, is capable of setting up an amount of corrosive mischief far greater than that arising from the action of sea water only, the increased loss varying from about 15 up to 50 per cent., according to the nature of the metals. From a reference to column 3 it will also be seen that the combined action of the sea and distilled water (although showing only such a slight saline composition and difference of salinity as indicated on Table B of analysis) whilst diffusing, produced an amount of local galvanic action in the same plate C, sufficient to induce therein much greater corrosion than in the case of plate B, although the latter was constantly immersed in the sea water (containing 2276·8 grains per gallon of sodium chloride), and was at the same time metal positive, as indicated by the galvanometer.

Table C.—Loss by Corrosion of Metals in Sea Water, and of the same Metal exposed to the Galvanic Action of diffusing Salt and Fresh Water during Fifty-two Weeks. Results in grains per square foot of surface exposed.

Description of metals.	Percentage of combined carbon.	Col. 1. Simple corrosion of the plate A in the sea-water vessel S.	Col. 2. Galvanic corrosion of the plate B in the sea-water vessel S.	Col. 3. Galvanic corrosion of the plate C in diffusing sea-water and distilled water.	Col. 4. Corrosion of the plate D in diffusing sea-water and distilled water.	Col. 5. Excess of loss from the action on plate C of diffusing salt and fresh water compared with loss in sea-water only. See column 1.
Common cast metal (No. 2)	0·670	235·42	240·07	289·03	236·75	53·61
"Soft" Siemens-Martin steel	0·170	259·94	262·38	395·52	344·34	135·58
Wrought iron.....	None	270·28	284·16	365·98	310·60	95·70
"Soft" cast steel....	0·460	278·54	343·98	349·29	249·38	70·75
"Soft" Bessemer steel	0·150	300·26	278·92	345·16	252·92	44·90
Best cast metal (No. 1)	0·390	308·68	326·99	354·39	269·61	45·71
"Hard" Bessemer ..	0·510	309·42	304·39	402·31	309·27	92·89

The experiments recorded in this and the former paper indicate therefore, that the tidal action on any vessel or metallic structure of sea and fresh water whilst diffusing, is (in the case even of the same

Table D.

Thames Water, January 15, 1878.									
London Bridge.			Greenwich.			Crossness.			
Depth from surface.	Tide.	Chloride of sodium in water.	Depth from surface.	Tide.	Chloride of sodium in water.	Depth from surface.	Tide.	Chloride of sodium in water.	
Surface . . .	1 hour flood	Grains per gal. 1·98	Surface . . .	2 hours flood	Grains per gal. 2·39	Surface . . .	4 hours flood	Grains per gal. 91·95	
Middle . . .	" "	3·46	Middle . . .	" "	2·47	20 ft. 0 in. . .	" "	109·50	
			27 ft. 0 in. . .	" "	2·80	40 ft. 0 in. . .	" "	117·46	
Surface . . .	½ hour ebb . .	2·36	Surface . . .	2 hours ebb. .	3·95	Surface . . .	½ hour ebb . .	104·48	
Middle . . .	" "	2·72	13 ft. 6 in. . .	" "	3·89	17 ft. 6 in. . .	" "	110·16	
Bottom . . .	" "	2·44	27 ft. 0 in. . .	" "	4·14	35 ft. 0 in. . .	" "	213·70	
			Surface . . .	3 hours ebb. .	3·05	Surface . . .	1½ hours ebb	101·43	
			11 ft. 0 in. . .	" "	4·86	17 ft. 0 in. . .	" "	130·35	
			22 ft. 0 in. . .	" "	2·93	34 ft. 0 in. . .	" "	189·18	

metal thus exposed to the simultaneous action of top and bottom waters) considerably more destructive in its nature and character than the action of sea water alone.

Moreover, the author has found it (in other experiments extending over long periods) to considerably exceed (in some instances varying from about 55 to 120 per cent.) the loss caused by galvanic action between dissimilar metals of the iron and steel group, in circuit in sea water.

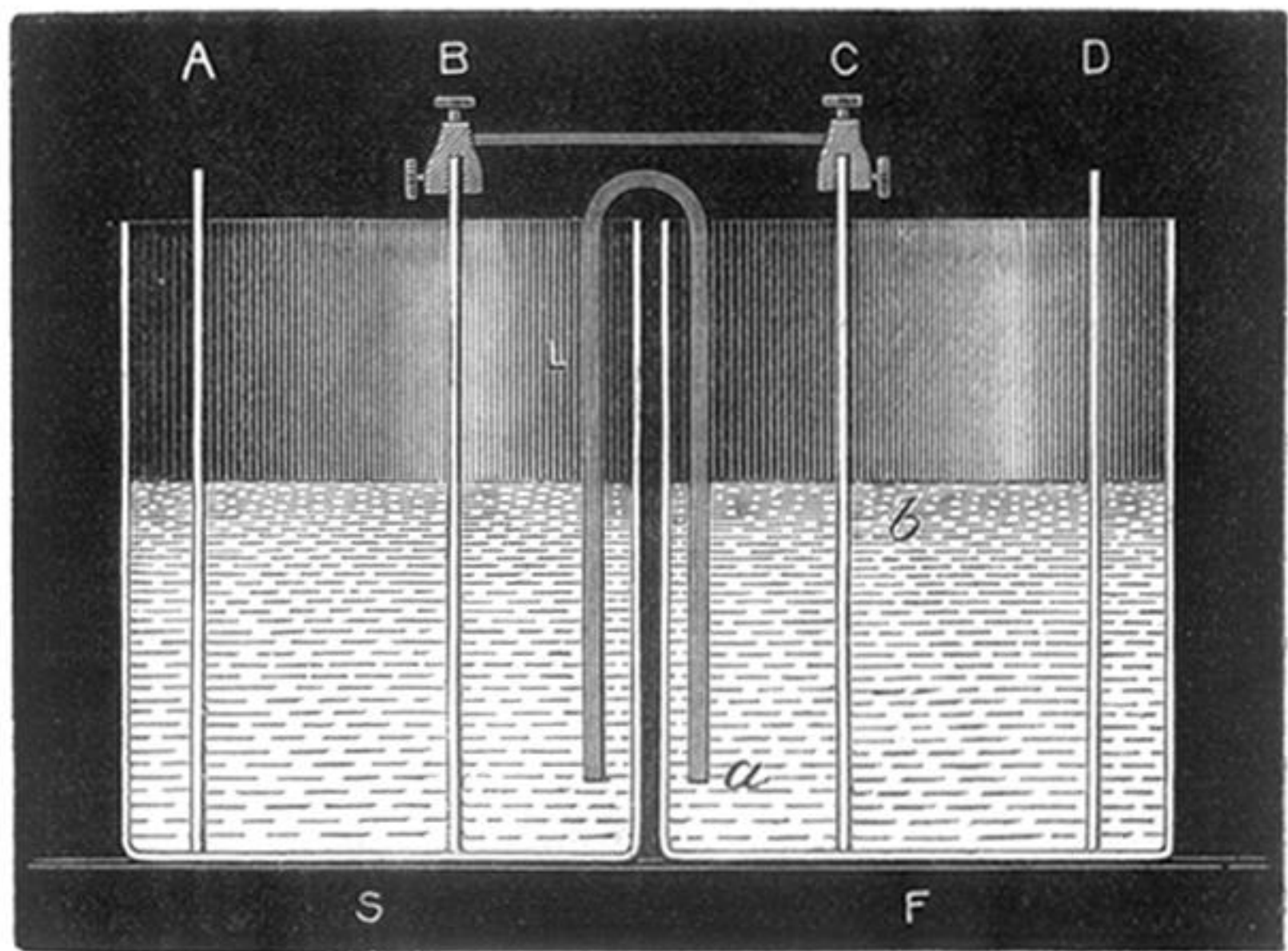
The arrangement of the waters in tidal streams and various effects consequent thereon form an intricate study; the author trusts, however, that the limited observations recorded in the present and the former paper may have afforded some information on the metallurgical aspect of the subject.

### Appendix.

The gradual rise and consequent inward flow of salt water and the outward flow of fresh water, has a general tendency to arrange the waters of a tidal stream into long, overlapping, wedge-like, layers or formations, the lower containing denser salt water and the upper more fresh water. This disposition of the waters is modified very considerably by currents, inter-diffusion, and numerous other conditions. The arrangement and diffusion of the salt and fresh water may not necessarily, at all places in the stream, be of an even character, almost isolated bodies of salt and fresh water not improbably accumulating in the numerous creeks, basins, or other indentations along the shores. The general contour of a stream, the influence of rainy or dry seasons (affecting the proportion of fresh water), the fact of its estuary being either long, deep, and narrow, affording little fall, or, on the contrary, of a wide shallow character, the states and times of tide, &c., and many other circumstances, also variously modify the diffusion results.

To illustrate further the basis and nature of this investigation, the author gives on Table D some typical analyses, selected from information relating to the disposition of the waters of tidal streams, kindly furnished by Dr. H. Clifton Sorby, F.R.S.; reference may also be made to the recent very interesting research "On the Salinity of the Firth of Forth," by Mr. Hugh Robt. Mill, B.Sc., F.C.S. (read before the Royal Society, Edinburgh, January 5th, 1885).

FIG. 1.



Sketch of one set of the Diffusion Cells.