March 26, 1885.

THE TREASURER in the Chair.

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

The Chairman announced that Mr. Walter White, after more than forty years of faithful service, had retired from the office of Assistant Secretary, and that Mr. Herbert Rix had been appointed to fill the vacancy.

The following Papers were read:—

I. "Observations on Variations of the Electromotive Force between Metals at High Temperatures in Fused Salts." By THOMAS ANDREWS, F.R.S.E., F.C.S. Communicated by Sir HENRY ROSCOE, F.R.S. Received March 12, 1885.

(Abstract.)

Reversals of the electromotive force between platinum and other metals in fused salts appear to have been noticed by Andrews about the year 1837, and in 1858 Hankel made some observations in this direction (Hankel, "Poggendorff's Annalen," 103, p. 612, 1858). Dr. Gladstone and Mr. Tribe ("Phil. Mag.," 1881) also found that a strip of silver plunged in molten AgI or AgCl, gives rise to a growth of silver crystals; the cause of this separation is the dissimilar temperature of different portions of the strip which produces thermo-currents. The present communication is an attempt to obtain quantitative estimations of the E.M.F., and of the extensive deviations from the normal electro-chemical positions of the metals (platinum and copper and platinum and iron) in fused salts, and the conditions of high temperature attending these reactions, which do not appear to have been previously determined. The cell for fusing consisted of a large platinum crucible (surrounded by known high temperatures) forming one element, a thick bent copper or iron rod inserted in the fused salt forming the other, or more frequently the copper plug of the Siemens' water pyrometer (which had been used in taking the time changes of temperature) was thus employed. A delicate galvanometer of known constants was used for taking the E.M.F., which was calculated from the observed deflections, in conjunction with the

ascertained resistances of the fused salts. The temperatures were determined in a large number of observations by the aid of a Siemens' water pyrometer. The salts employed as electrolytes were potassium carbonate, potassium chloride, potassium nitrate, potassium chlorate, potassium bisulphate, and sodium chloride, using platinum and copper or iron as elements. The action of two dissimilar salts in contact during fusion at 845° C. (K_2CO_3 and NaCl) on the same metal, platinum, was also observed, and considerable reversals of the E.M.F. to the extent of 0·37 volt occurred apparently from divergence of temperature in the relative rate of cooling from fusion of the two salts.

Table A* contains quantitative estimates in volts of the deviations of the E.M.F. from the normal. The results on this Table A show that by a regulation of the heat between the metals forming the elements, extensive deviations from the normal electro-chemical positions of the metals were obtainable, in connexion with some of the above fused salts, under the conditions of temperature recorded on the Tables A and B. In K_2CO_3, fused and resolidified (being then under the fusing point), a reverse E.M.F. of 1·037 volts was noticed (platinum positive), the current flowing from the platinum to the copper; on remelting the salt and equalising the temperature throughout to 845° C., an instant reversal of the direction of the current took place, the metals resuming their normal positions with an E.M.F. of 0·22 volt, platinum being now negative. In the case of platinum and iron, under the same conditions in the above salt, a total deviation of about 0·88 volt from the normal position was obtainable (platinum positive). In the water tube experiments greater divergences were noticed (see Table B). With potassium chloride, interchanges of position between the metals occurred, platinum at first being positive, with an E.M.F. of 0·318 volt, representing a total deviation of 0·94 volt. With potassium nitrate just before fusion point, an E.M.F. of 0·088 volt was observed (platinum positive); on the salt, however, reaching fusion, a reversal took place, the copper assuming its normal positive position.

Table B contains estimates of the temperature conditions attending the variations of the E.M.F. in fused K_2CO_3. Considerable reversals of the E.M.F. were noticed (platinum positive). The experiments in columns 1 and 3 show that a temperature divergence of about 260° C. between the platinum and copper, gave a reverse E.M.F. of 0·44 volt (platinum positive), a difference of 265° C. between platinum and iron gave a reverse E.M.F. of 0·24 volt (platinum positive), the E.M.F. reducing to a certain extent as the temperature difference decreased. To obtain a greater difference of temperature between

* The Tables A and B are not given in this abstract.

the metals (see columns 2 and 4), the copper element consisted of a bent pipe, immersed in the fused salt, through which water was kept flowing, the temperature of the copper being about 29° C. The platinum crucible was surrounded by temperatures from 549° to 879° C., a total variation of 850° C. between the two elements was obtained. A similar method was adopted in the platinum and iron experiments. A temperature divergence of about 518° C. between platinum and copper gave a reverse E.M.F. of 0·92 volt (platinum positive), but with the salt in liquid fusion (platinum at 879° C., copper at 29° C.) a reverse E.M.F. (platinum positive) of only 0·66 volt was obtainable. A temperature variance of about 522° C. between platinum and iron yielded an E.M.F. of 0·53 volt (platinum positive), but when the salt was in liquid fusion (platinum 879° C., iron 29° C.) a reverse E.M.F. (platinum positive) of only 0·40 volt was noticed. In a cell of this description, two opposing forces were observed in operation, the thermo-electric, contending at the higher temperatures with the normal electro-chemical action of the fused salt. The results of the water pipe experiments, recorded in detail on Table B, show that generally from some cause the extent of the reversed E.M.F. did not appear to correspond in exact proportion with the temperature divergences between the metals; this result may perhaps be accounted for by the electrolyte at the increased temperatures combating the thermo-electric influences, and commencing to restore the true electro-chemical equilibrium of the metals. A point of temperature is reached where the thermal effects counterbalance the normal electric action of the fused salt. There is apparently a powerful thermic influence, where equality of temperature does not obtain, reversing the E.M.F. from the metals, notwithstanding their immersion at high temperatures in such electrolytes as fused salts; this reversal of direction of the current in the case of K_2CO_3, continuing even with the salt at a temperature of 695° C., or above, the current passing from the hotter platinum to the colder copper. When, however, the point of fusion of the hot solidified salt is reached (834° C.), the metals, being at an uniform temperature therein, resume their true electro-chemical positions.

The foregoing and other repeated experiments appear to indicate that in the form of apparatus used by the author, these interchanges in the direction of the current between platinum and copper, or platinum and iron, were almost solely caused by differences of temperature surrounding the two metals forming the elements.