Addition of these four quantities gives 1.11 volts as the E.M.F. at 15° C. of the cell

Zinc | Normal zinc sulphate | Normal copper sulphate | Copper.

and the effect on this quantity of alterations in the concentration of the electrolytes may be calculated as described under heads (1), (2), and (3).

"ABNORMAL" E.M.F.

In contrast to the case of the Daniell's cell, where the total E.M.F. is practically the sum of the two individuals of Table 4, examples may be quoted where the allowance for difference in concentration of the electrolyte (in the case just calculated a mere correction) constitutes by far the largest term. Such, for instance, is the case in the combination*

$$\text{Ag} \mid 0{,}1 \text{ normal } AgNO_3 \mid \text{normal } KCl \mid AgCl \mid \text{Ag},$$

whose E.M.F. has been found to be 0.51 volt. This comparatively high value for a cell whose two electrodes are formed of the same metal depends on the fact that the osmotic pressure of the silver ions in the silver nitrate solution is very considerable; while in the silver chloride solution it is extremely small, both on account of the slight solubility of that substance, and because the dissociation of what silver chloride does dissolve is much reduced by the presence of the potassium chloride (see p. 238). When the cell is closed, the effect of the passage of the current is simply to remove silver ions from that solution in which their concentration is great to that in which it is small, and the E.M.F. of the cell will be

$$\pi = 0.0002\ T \log_{10} \frac{C_1}{C_2}$$

Where C_1, the concentration of the silver ions in the $AgNO_3$ solution, may be set (assuming complete dissociation) 0.1; while C_2, their concentration in the silver chloride solution, which, in the absence of potassium chloride, has been found† to be approximately 1.1×10^{-5},

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W. Nernst. Thereotische Chemie, Stuttgart, 1893, p. 569.

†*Kohlrausch and Rose*, Loeslichkeit schwer loeslicher Koerper, *Z. Ph. Ch.*, XII., 234, 1893, have estimated the solubility of silver chloride in water by determining the electrical conductivity of its solution, and calculating m (the quantity of salt dissolved) from the known velocities of the ions $\overset{+}{Ag}$ and $\overset{-}{Cl}$ by means of the equation:

Conductivity $m = (u + v)$. See page 232.