

As the individual electromotive forces of all ordinary voltaic batteries occur at the junction of

- (a) Metal with metal ;
- (b) Metal with electrolyte ;
- (c) Electrolyte with electrolyte,

it is possible from the data given above to calculate the E.M.F. of a large number of cells. For example, in the Daniell's element, the total E.M.F. is made up of

- (1) Zinc - Zinc sulphate solution.
- (2) Zinc sulphate solution - Copper sulphate solution.
- (3) Copper sulphate solution - Copper.
- (4) Copper - Zinc.

(1) Of these the first depends on the concentration of the zinc sulphate solution. If this contains 161 grammes Zn SO_4 per litre ("normal solution"), the E.M.F. will be 0.51 volts with the zinc negative [Table 4], which number will be greater if the electrolyte be more dilute, and conversely. The quantitative relation is given by equation (15c):

$$\pi = 0.0002 \frac{n_i}{n_e} T \log_{10} c + \text{constant}$$

(c being the concentration of the zinc sulphate in solution) the change in value of variable term on the right-hand side being obviously the quantity in question. Thus, diluting the electrolyte with an equal volume of water would change the E.M.F. to

$$0.51 + 0.0002 \times \frac{1.25}{2} \times (273 + 15) \log_{10} 2 = 0.51 + 0.0108$$

or about 0.52 volts, the zinc negative, as before.

(2) The second, on account of the approximate equality of the velocities of copper and of zinc [Table 2], will be negligible if the copper and zinc solution has the same concentration; if not, its value may be obtained from equation (18b).

(3) The third is similar to the first, for normal copper sulphate solution amounting to 0.60 volts, the metal positive; increase in concentration of the electrolyte increases this value, and conversely, according to the equation (15c), just quoted for zinc sulphate.

(4) The value of the fourth E.M.F. is given in Table 3. It may be neglected in comparison with the others, being less than the thousandth of a volt.

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