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Electrolytic Transfer

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A paper by Prof. Jos. W. RICHARDS, of Lehigh University, discussed the mechanism of electrolytic transfer with special reference to the phenomena in fused salts. The author emphasized the frequent deviations of a chemical compound from the simple or fixed atomic proportions. For instance, if iron pyrites FeS_2 is melted, sulphur leaves it and at a low temperature one has Fe_3S_4, Fe_5S_6, Fe_7S_8, or various approximations to FeS.

By an increase of temperature one passes by insensible gradations all the way to Fe_2S, and at electric furnace temperatures perhaps beyond this.

A chemical compound in absolutely atomic weight proportions is practically unknown in the whole class of melted mattes. In general a rather extensive study of fused salts and compounds leads him to regard fixed atomic weight prooprtions as the exception rather than the rule, in practical work.

If a tube full of smelted PbS is electrolyzed, lead is set free at one end and sulphur at the other. Now, Dr. Richards argues, the deficit of lead at the cathode is quickly distributed by diffusion throughout the whole electrolyte, while the deficit of sulphur at the anode is similarly rapidly distributed throughout the electrolyte. This distribution of the two deficits at the two electrodes is made possible by the known solubility of such intermediate products in the normal salt, and amounts to a virtual transfer of the two constituents from the whole mass of the electrolyte to the electrodes.

According to this view, the transfer in electrolysis is essentially solubility and diffusion of these slightly abnormal compounds formed by electrochemical action at the two electrodes. Dr. Richards therefore claims that the electrolytic transfer

occurs as the result of electrolysis and is not the preexisting mechanism of electrolysis.

In the discussion which followed Dr. Parsons suggested that to investigate the nature and mechanism of electricity one should begin with the simplest case, the transfer of electricity through gases, where the phenomena are already complicated enough, although much less in solutions.