ELECTROLYTIC SEPARATION OF METALS BY GRADED ELECTROMOTIVE FORCES.

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I give herewith some observations on a new method of electrolytic separation of metals by graded electromotive forces. This experimental physical work depends upon the fact that the salts of the different metals have different decomposing values. Freudenburg showed how it was possible to separate metals quantitatively in this manner.

It is only necessary to have two salts of the metals, which have decomposing values as far apart as possible. When an E. M. F. between these limits is passed through the cell, the metal with the lower decomposing value will separate; after that is separated the current will cease and it is only necessary to raise the E. M. F. in order to deposit the other metal.

When the concentration of the ions in the salt of the metal separated becomes decreased, as it almost invariably does, it is only necessary to raise the E. M. F. slightly. The amount of increase is small and may be readily calculated from the following formula:

$$\pi = \frac{R\,T}{N\,E_o} \log. \frac{P}{p}$$

If p decreases from 0.1 normal to 0.000001 normal, P must be increased 0.3 volts for a monovalent element and but half that amount for a divalent element. For example $AgNO_3$= 0.70 and $Pb(NO_3)_2$=1.52.

When these two solutions are together the Ag will be entirely decomposed by an E. M. F. of less than one volt; then the E. M. F. may be raised to 1.52 or more, and all the lead will be deposited. Separations are easily made in this way.

Below are given the separation values of a few ions. They

are based on the value of H taken as zero. That is if the value of H is added to that of OH, we will have the decomposition value of H_2O 1.68. These values are for molar concentrations.

Ag = — 0.78	1 = 0.52
Cu = — 0.5	Br = 0.94
H = + 0.0	O = 1.08 (In acids)
Pb = + 0.17	Cl = 1.31
Cd = + 0.38	OH = 1.08 (In acids)
Zn = + 0.74	OH = 0.88 (In base)

The table is applied to the quantitative determination of Cl, Br, and I, in solutions.

The minimum E. M. F. of decomposition of this system for a solution of Ag and separation H, is given by the following equation:

$$\pi = 0.5075 \log. \frac{P_1}{p_1} - 0.0575 \log. \frac{P_2}{p_2}$$

at 17°, when P_1 and P_2 are the electrolytic solution pressures of the Ag and H, p_1 and p_2 being the osmotic pressures of the ions Ag and H.