SOME NOTES ON SEPARATION OF METALS.

It may be stated in this connection that no change was observable in the color of the butter from feeding cotton seed and cotton seed meal. The samples, still in the laboratory, are all of a beautiful golden yellow.

It is proper to state that the analytical work in the above tables was done by Dr. J. T. Anderson, first assistant in the chemical laboratory.

AUBURN, ALA., March 27, 1891.

"SOME NOTES ON ELECTROLYTIC QUANTITATIVE" SEPARATION OF METALS."

BY T. O'CONNOR SLOANE, PH. D.

It may seem somewhat presumptuous after Classen's classic work in electrolytic analysis, to offer any suggestions as to the conducting of this class of quantitative determinations. But there is one point in the work which it may safely be said has been to a certain extent neglected. This point is the influence of electromotive force, or of difference of potential upon the separations.

In Classen's work upon the subject the voltage of the circuit is duly considered, and an elaborate rheostat for regulating the voltage within somewhat crude limits $(\frac{1}{2}$ volt) is described. This is in one of the introductory chapters. The rheostat is for use with a 600 watt dynamo. But the author also mentions batteries and describes his method of conducting determinations with these sources of electromotive force. The current strength is then the standard, and it is determined by the volume of oxyhydrogen gas, which the current can liberate in a definite time. In other words, the amperage of the current alone receives direct attention. By using the same sized electrodes, the author states, the conditions are kept sensibly the same. Here we have an indirect recognition of the influence of electromotive force. But the attempted

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maintenance of the most uniform conditions is a poor reliance. The conditions will inevitably vary and the temperature of the room and gradual change of the nature of the solution operated on will cause variations in resistance that will affect the difference of potential. To show how little regard is paid to voltage, we are directed in iron determinations to use two and sometimes three Bunsen cells. Any change in the number of cells in series would cause great variations in the voltage, in the case cited about 50%. If the cells were kept in parallel and any resistance, such as that of a voltameter, were in series with the decomposing apparatus, a great variation in voltage would even then ensue by changes in the number of cells.

The object of these notes is to plead for a greater recognition of the influence of difference of electric potential in analytical work. The facts of the case are these : For the decomposition of every solution a definite and absolutely fixed voltage is required. The strength of current affects only the condition of the deposit. Thus a current of any number of amperes might be passed through acidulated water without decomposing it until the voltage passed a fixed point when decomposition would at once begin. A single gravity cell, large or small (sulphate of copper-zinc-copper couple) cannot decompose water because its voltage is too low. The minutest bichromate cell will at once begin to decompose it because its voltage is high enough.

Again, the amperage of the current should not be broadly stated without reference to absolutely fixed conditions of electrodes. The proper way would be to state it as referred to unit area of cathode and anode. Probably the cathode reference would be all that is needed. As ordinarily put the cathode is supposed to be a platinum dish of more or less definite size, filled with a variable depth of fluid, and the electrolytic gas set free in one or more minutes is given. All this tells nothing.

It would seem obvious that, a definite and absolutely fixed difference of potential being required for the decomposition of each compound, the voltage could be made the basis for analytical work. It would be possible to effect successive separation of metals from the same solution by modifying the voltage, starting, of course, with the lowest. How far the precipitation of mixed metals, so called alloys, would interfere with such attempts is not definitely recorded. It amounts to nothing to state, as is done, that a weaker current than is required for iron or some other metals, will precipitate copper. The strength of the current has nothing to do with it. It is the difference of potential that affects the result. The varying of such difference corresponding in a general way with the strength of the current, as the operations were conducted, has doubtless occasioned the confusion.

In stating the results of or giving directions for conducting electrolytic separations, two factors should always be stated. One is the difference of potential, the other the amperage per unit area of cathode. Then something definite would be known. It seems probably that by working on these lines, some exceedingly interesting results in the way of double decompositions as well as of separations, might be obtained.

Should any such result be obtained as the determining of a series of potential differences available for separations of metals from single solutions it would be highly interesting. The heat of combination of a vast number of compounds has been obtained and is readily reduced to volts, but such reduction is theoretical and does not accurately hold for all cases. The principal trouble would lie in the regulation of the voltage. But at the least there seems ground for research in the direction here suggested.

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