

700°. After cooling, the mass is extracted with hot water, filtered, and the chlorine determined by either Mohr's or Volhard's method. The results obtained average about 0.2 to 0.3% low, indicating a small loss by volatilization, but are sufficiently accurate for most purposes. Should greater accuracy be desired, the method of Lamb and Marden¹ of heating the perchlorate alone in a glass test-tube and retaining the fumes evolved with a plug of asbestos wool, may be employed. When manganese dioxide is used, a blank is necessary inasmuch as commercial as well as native manganese dioxide always contains a small amount of chlorine.

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Electrolytic Reduction of Chromic Chloride to the Divalent Salt.¹—

The problem of chromium reduction arose in connection with the work done at the Edgewood Laboratory on a method for producing ethylene from acetylene by the use of a solution of chromous chloride as a reducing agent. It was proposed to convert the chromic chloride produced by the acetylene treatment back to the divalent salt by means of electrolytic reduction. The investigations described in the present communication were undertaken to find conditions whereby it would be possible to obtain satisfactory yields of chromous chloride.

In the electrolytic reduction of chromic to chromous chloride the principal source of inefficiency is the production of hydrogen gas at the cathode. In some of our preliminary attempts at reduction an insoluble deposit formed on the cathode. The formation of such a coating of course represented inefficiency as far as the production of chromous chloride was concerned. However, the conditions under which the experiments reported herewith were carried out were such as to prevent the formation of any such deposit, and we may therefore regard the production of hydrogen gas as the only source of inefficiency in these particular experiments. Just what caused the deposit to appear in the preliminary work is unknown, but it may have been due to impurities in the chromic chloride solution, or to too high current density when the chromic concentration of the solution became small.

The following procedure was adopted as a means of determining the part of the current used for reduction purposes: the hydrogen evolved from the cathode in a given time and by a known amount of current was measured and reduced to standard conditions; the total hydrogen which would have been evolved by the current, had none of it been used for reduction pur-

¹ Lamb and Marden, *THIS JOURNAL*, **34**, 812 (1912).

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poses, was calculated from the known current amperage; the difference between this volume and the volume actually evolved represented the amount used in reducing chromic chloride and was a measure of the efficiency. The results obtained by this procedure were found to check those obtained by determining the chromous chromium produced by a given amount of current.

The reduction was carried out in an ordinary 2-compartment cell, with a spiral spongy lead cathode surrounded by 5 graphite anodes. The 2 compartments were separated by a porous cup of rather fine structure. In order to obtain the best results it was found essential to provide for a stirrer in the cathode compartment.

Numerous experiments were performed with results similar to those reported in Table I. The efficiency was good at the beginning of the reduction when the concentration of chromic chromium was high, but as this was consumed the efficiency fell off rapidly. In some experiments where the reduction was carried on until 86% of the chromium was reduced, only 9% of the current was being used to reduce the remaining chromic chromium.

It seemed that the efficiency might be a linear function of the chromic-ion concentration. In order to prove this the action was assumed to be that of nascent hydrogen produced by the current at the cathode on trivalent chromium, thus, $\text{Cr}^{+++} + \text{H} \rightarrow \text{Cr}^{++} + \text{H}^+$. When hydrogen gas was being given off at the cathode even in small quantities we have assumed that the concentration of nascent hydrogen was constant and at its maximum. If this is true and if the reaction proceeds as indicated, the rate of reduction would be proportional to the concentration of chromic chromium,

thus, $\frac{dx}{dt} = K(a-x)$, where x is the amount of chromous chromium formed

in t minutes, and a is the original concentration of trivalent chromium. Beginning at the point where appreciable inefficiency appeared, the K value in the above equation was calculated from the data of Table I and tabulated in the column marked K . In the same way calculations were made on several other experiments, all of which indicated that the rate of reduction was a linear function of the chromic chromium concentration.

Now, if we bring this theory to bear on the problem of securing high efficiency, we see at once that the reduction will theoretically proceed as fast when we have only a small excess of hydrogen as when there is a large excess. In other words, the rate of reaction as determined by the concentration of trivalent chromium prevents the use for reduction purposes of more than a certain amount of current at any given time, and if we use more than this we are certain to decrease the efficiency. The current employed then may be very high at first, but should be decreased during reduction in proportion to the decrease in chromic concentration.

TABLE I
REDUCTION EMPLOYING CONSTANT CURRENT DENSITY
Volume of cathode solution at start, 225 cc.
Grams of Cr per cc., 0.11031
Grams of Cr⁺⁺ per cc., 0.00128
Total cathode surface, 1.24 sq. dm.

Time	Amperage	Hydrogen evolved Cc.	Total hydrogen Cc.	Efficiency %	Cr as Cr ⁺⁺ %	K
9.47-11.05	1.6	0.0	...	100.0	17.4
11.05-11.35	1.6	0.4	334.1	99.9	23.6
11.35-12.05	1.6	0.7	334.1	99.8	29.9
12.05-12.35	1.6	0.9	334.1	99.7	36.1
12.35- 1.05	1.6	7.5	334.1	97.8	42.2	0.00335
1.05- 1.35	1.6	34.2	334.1	89.8	47.8	0.00338
1.35- 2.05	1.6	68.4	334.1	79.5	52.8	0.00336
2.05- 2.35	1.6	97.5	334.1	70.8	57.2	0.00334
2.35- 3.05	1.6	115.8	334.1	65.3	61.3	0.00334

Several experiments according to this method have shown that by reducing the amperage to correspond with the decrease in chromic chromium, an efficiency of 96% can be maintained over the period required to reduce 87% of the chromium; whereas, by holding the amperage constant only 53% efficiency could be obtained for the same amount of reduction.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]
COMPOUNDS OF TELLURIUM TETRABROMIDE WITH ORGANIC BASES¹

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This investigation was undertaken with a twofold purpose in view: (1) to prepare compounds of tellurium tetrabromide with organic bases which will be utilized in further research work, and (2) to prepare selenium and tellurium dyes analogous to the class of sulfur dyes by substituting the element selenium or tellurium in place of sulfur, as, for example, in the preparation of sulfur black, etc.

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² This report represents an abstract of a thesis presented by R. F. Dunbrook, in partial fulfilment of the requirements for the degree of Master of Science, September, 1921.