

The effect of the electrical discharge on the liquid products has been studied.

In contrast to the reaction under influence of alpha-radiation, acetylene is hydrogenated in the electrical discharge to some extent.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KENTUCKY]

THE SODIUM COULOMETER

By OLUS J. STEWART

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Several years ago R. C. Burt¹ effected the electro-deposition of elementary sodium within incandescent lamp bulbs lowered into baths of molten sodium nitrate. Investigation showed that the bulbs were not appreciably attacked by the bath and that the process followed Faraday's law with an accuracy of at least 0.2%. Burt urged the use of the instrument as a voltameter which he² later modified "by using metal contact with glass instead of thermoionic emission." Further description of the instrument was omitted except for the statement that "the process yields results which are certainly correct to 1:2000 and probably to 1:6000."

Advantages uniquely held by the sodium voltameter made it desirable to investigate its accuracy further.

The work began with Burt's original voltameter, which was soon abandoned in favor of an instrument containing mercury in contact with ordinary glass. The quantity of sodium deposited was determined either by weighing or by dismantling the instrument and titrating the alkali with standard acid. Numerous objectionable features, such as the high density of mercury, the low solubility of sodium in mercury, the proneness of mercury to "bump" and the low electrolytic conductivity of ordinary glass led to the production of a superior type of instrument.

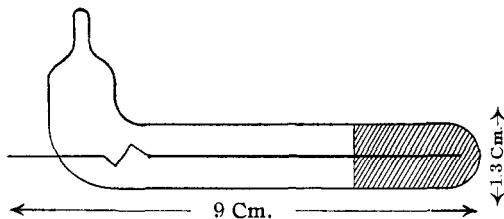


Fig. 1.

This coulometer, Fig. 1, is made of glass (about 1.4 mm. thick) designated by the Corning Glass Works, "Corning clear, soft lime tubing, No. 015." The platinum wire, sealed through the glass and coiled for flexibility, is brazed to a stout nickel wire

extending to the bottom of the tube. Each electrode contained 15 g. of cadmium but the anode also contained 0.5 g. of sodium. Evacuation,

¹ R. C. Burt, *J. Opt. Soc. Am.*, **11**, 87 (1925).

² R. C. Burt, *Phys. Rev.*, **27**, 813 (1926).

sealing with a flame, washing, wiping with a damp cloth and drying in a desiccator prepared it for weighing. To place the instrument in service, it was suspended from a glass rod and lowered cautiously into a bath of sodium nitrate whose temperature remained at about 340° . The duration of each experiment was three hours and a 48-volt battery furnished the current.

Four types of quantitative work were carried out and the data have been listed in the tables, which are self-explanatory.

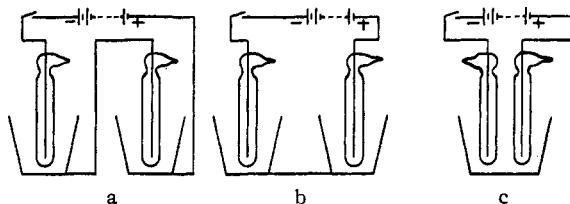


Fig. 2.

TABLE I
COULOMETERS OPERATED IN SERIES FOR THE DEPOSITION OF SODIUM
Circuit (a), Fig. 2

Expt.	Cell 1, sodium, g.	Cell 2, sodium, g.	Difference, g.	Mean differ- ence, %
1	0.26262	0.26262	0.00000	0.000
2	.34384	.34391	.00007	.010
3	.60646	.60653	.00007	.006
4	.31648	.31656	.00008	.013
5	.06513 ^a	.06514 ^a	.00001	.008
6	.26542	.26537	.00005	.009
7	.33168	.33171	.00003	.005
8	.33075 ^b	.33073	.00002	.003
Total	2.52238	2.52257	.00019	.004

^a Weights of sodium remaining in the cells after electrolytically removing a portion of the metal previously deposited.

^b The bath in which Cell 1 was operated consisted of 230 g. of sodium nitrate and 11.5 g. of potassium nitrate. There was no evidence of potassium having passed through the glass.

The facts that used cathodes were slightly etched while anodes retained their polish and that unusually high temperature permitted thin softening outer walls of microscopic gas pockets to bulge on the cathode only, suggest electrolytic loss of silicate ions from the cathode surface. Added to this qualitative evidence is that of a quantitative nature recorded in the tables where it is seen that coulometers operated in series under identical electrical conditions yielded concordant results, anodic results closely agreed with those of the silver coulometer, and the difference between anodic and cathodic figures approximated the cathodic error. Therefore,

TABLE II
COULOMETERS OPERATED IN SERIES FOR THE REMOVAL OF SODIUM. THE CIRCUIT OF
FIG. 2 (a) WAS USED BUT THE CURRENT WAS REVERSED

Expt.	Cell 1 sodium, g.	Cell 2 sodium, g.	Difference, g.	Mean differ- ence, %
9	0.25134	0.25142	0.00008	0.016
10	.32083	.32069	.00014	.022
11	.20406	.20405	.00001	.003
12	.20962	.20958	.00004	.010
13	.35975	.35977	.00002	.003
14	.42817	.42828	.00011	.013
15	.32492	.32501	.00009	.014
16	.33818	.33830	.00012	.018
17	.33156	.33157	.00001	.002
Total	2.76843	2.76867	.00024	.004

TABLE III
COULOMETERS OPERATED IN SERIES, ONE FOR THE DEPOSITION, THE OTHER FOR THE
REMOVAL OF SODIUM, EITHER IN THE SAME OR IN SEPARATE BATHS. CIRCUITS (b)
AND (c) FIG. 2

Expt.	Cell 1, sodium deposited, g.	Cell 2, sodium removed, g.	Difference, g.	Mean difference, %
18 ^a	0.19092	0.19111	0.00019	0.050
19 ^b	.14962	.14977	.00015	.050
20 ^b	.12092	.12109	.00017	.070
21 ^a	.31447	.31478	.00031	.049
22 ^a	.34347	.34380	.00033	.048
Total	1.11940	1.12055	.00155	.069

^a Coulometers in separate baths. ^b Coulometers in same bath.

TABLE IV
SODIUM AND SILVER COULOMETERS OPERATED IN SERIES

A	B, g.	C, g.	D, g.	E, %	F, g.	G, g.	H, %	I, %
22	0.34347	0.34380	0.048	1.61262	0.34377	0.004	0.044
1633818	0.33830	.018	1.58668	.33824	.000	...
1733156	.33157	.002	1.55569	.33163	.011	...

A, no. of experiment. B, weight of sodium deposited. C, weight of sodium removed. D, weight of sodium removed. E, mean difference in weights of deposits or removals. F, weight of silver. G, calculated weight of sodium equivalent to the silver. H, mean difference between the actual weight of sodium removed and the calculated weight of sodium equivalent to the silver. I, mean difference between the actual weight of sodium deposited and the calculated weight of sodium equivalent to the silver.

the electrochemical process taking place in the sodium coulometer is completely reversible, the cause of the cathodic error now being understood.

Reagents and Apparatus

Burt¹ pointed out that purified reagents are not required and we found that sodium nitrate, used repeatedly in the iron dishes, acquires but a trace of alkali and reducing material. Reagents for the silver coulometer

were purified as in a previous research³ but the silver required neither fusion in hydrogen nor heating in vacuum. A large suitably shaped button was reserved for anodic purposes and the remainder was converted to nitrate with the precautions required in precise work. To insure removal of acid the dry salt was ground in an agate mortar and heated for several hours at 170°. Electrolyte sufficient for the siphon type silver coulometer was prepared by dissolving 15 g. of silver nitrate in 120 ml. of water. The adherent, non-striated, brilliantly crystalline deposits of silver, free from anodic slime, were carefully washed, allowed to soak for eight hours, and dried at 170°. A correction⁴ of 0.004% was applied except that in Expt. 17 the correction for moisture was determined by heating the deposit to redness.

All weighings were made by substitution for similar counterpoises and the weights were standardized to hundredths of a milligram by the Richards method.⁵ In weighing, precautions were taken to avoid errors due to electrical charges on glassware, bending of the balance beam, illumination and changing temperature.

Vacuum corrections were applied as follows:

Silver.....	0.000031 g. per g.
Sodium.....	.000062 g. per g.

The vacuum correction for sodium is based solely on the densities of air and of the gold weights for the sodium displaced no air.

Summary

1. A sodium coulometer of comparatively high conductivity has been described.
2. Anodic sodium coulometers were found to yield more accurate results than the cathodic type.
3. An explanation of the inaccuracy of earlier sodium coulometers has been offered.
4. The anodic sodium coulometer was found to yield results accurate at least to 1:10,000.

LEXINGTON, KY.

³ Stewart and James, *THIS JOURNAL*, **39**, 2605 (1917).

⁴ See Rosa and Vinal, Bureau of Standards Scientific Paper No. 285.

⁵ T. W. Richards, *THIS JOURNAL*, **22**, 144 (1900).