ENGELHARDT:

ELECTROLYSIS OF WATER

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—ON—

APPLIED ELECTROCHEMISTRY

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MONOGRAPHS ON APPLIED ELECTROCHEMISTRY.
VOL I.

THE

ELECTROLYSIS OF WATER

PROCESSES AND APPLICATIONS

BY

VIKTOR ENGELHARDT

CHIEF ENGINEER AND CHEMIST OF THE SIEMENS & HALSKE
CO., LIMITED, VIENNA.

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With 90 Figures and 15 Tables in the Text.

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AUTHOR'S PREFACE TO GERMAN EDITION.

Corresponding with the rapid growth which the application of electrochemical processes have shown in practice, the literature of this field has grown remarkably in the last ten years of the past century. This literature has, however, in spite of the existence of present German and other treatises and the regularly appearing periodicals, yet exclusively remained a simple current report. Those works which have appeared, which in a concise form treat of the larger field of applied electrochemistry, are for the most part primarily intended for students and therefore have a general character. Special treatises on applied electrochemistry which will treat of their subjects exhaustively in all directions are, with the very few exceptions, not in existence.

This deficiency is, however, easily explainable if we consider more closely the way in which electrochemical processes reach commercial applications.

We can, on the whole, if we leave out of consideration the electrochemical sources of the current, which form a group of themselves, divide these electrochemical processes into two principal classes.

One series of processes which we may designate as electrochemical installation-processes, have as their object, without forming a branch of manufacture themselves, to introduce technical improvements or economies in the existing industries and processes.

What appears on such processes in literature is only in rarest cases published by the industries making use of the processes themselves; but in the main by the patentees of the process in question, who are in most cases, identical with the manufacturers of the machinery and apparatus necessary for the practice of the process. Since it is in the interest of the latter to erect as many plants as possible, the literature must be exploited for advertising purposes. The description given of the form of apparatus is usually only diagrammatic, and often has the object of deceiving those who should hope to work in the same direction. As an example of such electrochemical installation we may quote the electrolytic purification of beet-sugar solution, the so-called electrical bleaching, many applications of ozone, the electrolytic decomposition of water, some metallurgical refining processes, etc.

The second large group are the real electrochemical manufacturing processes like the chlorine and alkali industry, the manufacture of chlorates, carbides, most of the metallurgical applications of electrochemistry and the like. In these processes the withholding of published information is greater than in the previous ones. With the exception of the patent specifications, very little is made public. Every practical electrochemist knows how far the principles described in the patent specifications are different from the real applications in practice.

In the collection of "Monographs of Applied Electrochemistry," the first volume of which is herewith published, it will be the object to set forth detailed and most authentic reports in the field of applied electrochemistry. These monographs will not be general compilations on the present condition of the several fields of applied electrochemistry, but exhaustive special reports, in which the entire historical development will be set forth, and a good review of the most important patent literature made. An endeavor will further be made to modify, as far as possible, the conservatism of the commercial circles and to give as far as possible commercial data, such as cost of plant and operation, commercial conditions and the like.

Our co-operators, who on the one side are instructors in electrochemistry in the technical colleges, in close connection with the pioneers of electrochemistry, on the other side practical electrochemists in successful commercial work, permit the hope of our success to appear well-founded.

Yet we do not like to narrow the boundaries which we will observe in the "Monographs of Applied Electrochemistry." How much work which was undertaken with a purely theoretical interest really provides a rich source of valuable material for industrial applications! How valuable for the practical man would be the exhaustive reports on the special conditions of work and production in the different countries in which electrochemistry flourishes!

We therefore hope that the collection of treatises whose publication is now begun will be a welcome assistance to our professional men in their work.

Surely we will reach this goal if not only the above-named cooperators but all professional men will aid us by communicating their experiences and reporting any modifications or mistakes.

For assistance rendered in this direction we therefore offer our best thanks in advance.

VIKTOR ENGELHARDT.

Vienna, January, 1902.

TRANSLATOR'S PREFACE.

To any one in the least conversant with the rapid recent growth of applied, as well as theoretical electrochemistry, no apology or explanation will be necessary regarding the timeliness of translating the present series of monographs. A considerable proportion of the English-speaking electrochemists can read the German text, but a still larger proportion cannot, and that the latter class may have access to the thoughts and ideas of these monographs, is the purpose of these translations.

The present work is rich in suggestions of ways and means for accomplishing difficult ends, in electrochemical operations; its perusal will be found instructive and stimulating to the electrochemist in any line. It is therefore of far greater value than a mere code of operations for producing hydrogen and oxygen, as will be recognized by the reader as soon as he reads into the text.

The translator wishes here to acknowledge his indebtedness to W. S. Landis, E.M., for his considerable assistance in taking down the translation and reading proof-sheets.

JOSEPH W. RICHARDS.

Metallurgical Laboratory,
Lehigh University,
Sept. 22, 1903.

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IV. APPLICATIONS:

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I. HISTORICAL REVIEW.

INTRODUCTION.

Beginning as we do the collection of "Monographs of Applied Electrochemistry," with a description of the electrolysis of water, this is not done under the assumption that the processes included therein are of the highest interest among present electrochemical questions, from a technical standpoint, but out of the feeling of thankfulness towards those investigators, who more than one hundred years ago first worked with the chemical action of the electric current and first recognized such in the electrolytic decomposition of water.

THE DISCOVERY OF THE ELECTROLYTIC DECOMPOSITION OF WATER.

Even the investigations on the decomposition of combined bodies by the electric spark, which preceded a knowledge of the Voltaic pile, had their first undoubted results in the decomposition of water. Paets van Troostwijk and Deimann communicated in the year 1789 in a letter to de la Metherie, their observations, according to which they had decomposed water by the electric spark into combustible air and vitalized air.[1]

J. W. Ritter in the year 1798 recognized also the relation between chemical and electrochemical phenomena, but the electrolytic action could not be further investigated until a more powerful means was at hand than the simple pairs of metallic plates known in 1800. The Voltaic couple first gave to investigators of that time the assistance which was needed.[2]

As Ostwald says in his classical work[3] the chemical action of the Voltaic pile escaped observation by Volta himself.

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[1] Ostwald: Elektrochemie, ihre Geschichte und Lehre 1896, 21. Observations sur la physique etc., **35**, 1789, 369–378. Grens Journal der Physik., **2**, 1790, 130. Kopp: Geschichte der Chemie, 1845, III, 274.

[2] Phil. Trans., 1800, II, 405–431. Ostwald: Elektrochemie, ihre Geschichte und Lehre, 1896, 115.

[3] Ostwald: Elektrochemie, ihre Geschichte und Lehre, 1896, 129.

Ostwald writes about this: "The very evident oxidation phenomenon at the plates was wholly left out of consideration by Volta; indeed from the researches which he reports it may be seen that he took wires from the end of his pile and dipped them into water, so that necessarily electrolysis and evolution of gas must have taken place, but, although describing with the greatest care every other single phenomenon he makes no single suggestion that he had seen any chemical action."

Ritter was indeed, as is shown by the investigations of Ostwald, the first to observe decomposition of water by the electric current.[1]

For a long time the priority of this discovery was ascribed to the Englishmen Nicholson and Carlisle. Kopp[2] writes as follows: "In the year 1800 the Englishmen Nicholson and Carlisle, in the course of investigations made together, observed that in discharging the Voltaic pile through water, evolution of gas takes place and that the water was decomposed into its constituents by electricity, evolving them both as gases as long as the conducting wires in contact with the water consisted of an unoxidizable metal. These are the first recognitions of galvanic electricity as a chemical agent."

Landriani was led by the publication of Nicholson's[3] observations to repeat the experiment, and it was through this that Volta first knew of the phenomenon which had been discovered by the use of his pile. For its historical interest a picture of the apparatus as used by Landriani is reproduced in Fig. 1.[4]

Quite a number of investigators followed this line of investigation. The puzzling appearance of acids and bases at the electrodes coming from the small amounts of impurities in the water, led to the investigation of Davy, and to the accu-

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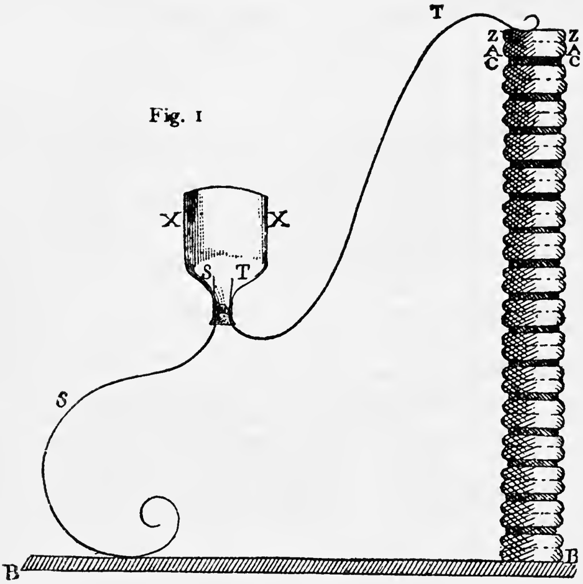
[1] Ritter: Beiträge zur Kenntnis des Galvanismus, 1800, **1**, 252. Voigts Magazin für den neuest. Zust. d. Naturk, 1800, **2**, 356. E. Hoppe: Elektrotech. Zeitschr., 1888, **9**, 36.

[2] Kopp: Geschichte der Chemie, II, 1844, 330.

[3] Nicholson's Journal of Nat. Philos., 1800, **4**, 179.

[4] Ostwald: Elektrochemie, ihre Geschichte und Lehre, 1896, 132.

Fig. 1



rate knowledge of this phenomenon is to be ascribed the final discovery of the alkali metals. Others constructed apparatus to keep the products of decomposition separate and to learn the composition of water from the relations of the volume of the gases. Others finally busied themselves with the qualities of the gases evolved during electrolysis. Since in the electrolysis of dilute sulphuric acid ozonized oxygen is evolved, many investigators ascribed to the evolved hydrogen especially active qualities. The works of Osann[1], Jamin[2], Brunner,[3] and Crova,[4] in this direction were disputed by de la Rive[5] and A. Brewster.[6]

[1] Pogg. Ann., **95**, 311; **96**, 510 (1855); **97**, 327 (1856). J. prakt. Chem., **92**, 20, 1864.

[2] Compt. rend., 1854, **38**, 443.

[3] Mitt. naturf. Gesellsch. Bern., 1864, **555**, 17.

[4] Mondes, 1864, **5**, 210.

[5] Arch. ph. nat., 1854, **25**, 275.

[6] Bull. Soc. Chim., 1866, **8**, 23.

OLDER LITERATURE.

In the following table is given a compilation of the most important older literature concerning the electrolysis of water, taken from Webb's index and partially enlarged.

TABLE I.

Year.	Author.	Journal.	Vol.	Page.
1789	Troostwijk	Journal de physique, Rozier, Paris	2	130
1797	Pearson	Philosophical Transactions of the Royal Society, London	90	188
1800	Nicholson	Journal of Natural Philosophy, Chemistry and the Arts, London	4	183
1801	Gautherot	Annales de chimie et physique, Paris	39	203
	Gilbert	ditto	41	107
	Pfaff	Gilbert's Annalen	7	363
	Cruikshank	ditto	7	91
	Klingert	ditto	7	349
	Simon	ditto	8	22, 37
	Davy	ditto	7	114
1803	Simon	Annales de chimie et physique, Paris	45	182
1804	Wilkinson	Journal of Natural Philosophy, Chemistry and the Arts, London	9	243
1805	Sylvester	ditto	10	106
1806	Grotthus	Annales de chimie et physique, Paris	58	10
1807	Alemani	ditto	65	323
1808	Davy	Gilbert's Annalen	28	1, 161
1811	Anderson	Journal of Natural Philosophy, Chemistry and the Arts, London	30	183
1812	Murray	ditto	31	87
1830	Bonijol	Bibliothèque universelle des sciences, Genf	(1830)	Oct.
1832	Bonijol	Journal of the Royal Institution of Great Britain	1	293
1837	Pouillet	Comptes rendus des séances de l'Académie des Sciences, Paris	4	785
1839	Becquerel	ditto	8	497
	Grove	ditto	8	802
	Jacobi	London, Edinburgh and Dublin Philosophical Magazine	15	161
1841	Becquerel	Archives de l'électricité, Genf	1	281
1842	De la Rive	ditto	2	468
	Pearson	Annals of Electricity, London	9	496
	Weber	Archives de l'électricité, Genf	2	661
	Wollaston	Annals of Electricity, London	9	518
1845	Millon	Archives de l'électricité, Genf	5	303
1851	Vigau	Comptes rendus des séances de l'Académie des Sciences, Paris	34	734
1852	Jamin	ditto	38	390
	Leblanc	ditto	38	444
1853	Kard	London, Edinburgh and Dublin Philosophical Magazine	6	241

Year.	Author.	Journal.	Vol.	Page.
	Shepard	British Patent Reports	(1853)	—
1854	Callau	London, Edinburgh and Dublin Philosophical Magazine	7	73
	Connell	ditto	7	426
	De la Rive	Archives des sciences physiques et naturelles, Genf	25	275
	Jamin	Comptes rendus des Séances de l'Académie des Sciences, Paris	38	443
	Dumas	ditto	38	444
	Foucault	Archives des sciences physiques et naturelles, Genf	25	180
	Leblanc	Comptes rendus des séances de l'Académie des Sciences, Paris	38	444
	Soret	Archives des sciences physiques et naturelles, Genf	25	175
1855	Buff	ditto	31	198
	Buff	Annalen der Chemie u. Pharmacie, Heidelberg	93	256
	Osann	Annalen der Physik u. Chemie, Poggendorf, Berlin	95 96	311 510
1856	Andrews	Annales de chimie et physique, Paris	50	124
	De la Rive	Comptes rendus des séances de l'Académie des Sciences, Paris	42	710
	Despretz	ditto	42	707
	Osann	Annalen der Physik u. Chemie, Poggendorf, Berlin	97	327
	Sorel	Annales de Chimie et physique, Paris	45	11
	Soret	Archives des sciences physiques et naturelles, Genf	31	204
	—	Journal für praktische Chemie, Erdmann, Leipzig	67	173
1857	Breda	Annalen der Physik und Chemie, Poggendorf, Berlin	99	634
	Geuther	American Journal of Science and Arts, New Haven	28	281
1858	Fonvielle	Comptes rendus des séances de l'Académie des Sciences, Paris	47	149
1859	Friedel	Annalen der Chemie und Pharmacie, Heidelberg	112	376
1861	Andrews	Journal of the Chemical Society, London	13	344
1864	Osann	Journal für praktische Chemie, Erdmann, Leipzig	92	20
	Brunner	Mitteilungen der naturforschenden Gesellschaft, Bern	555	17
	Crova	Mondes	5	210
1866	Brewster	Bulletin de la Société Chimique, Paris	8	23
1867	Hofmann	ditto	10	228
1868	Bourgoin	ditto	10	206
	Rundspaden	Annalen der Chemie und Pharmacie, Heidelberg	151	306

Year.	Author.	Journal.	Vol.	Page.
1869	Gerland	Annalen der Physik und Chemie, Poggendorf, Berlin	137	552
	Graham	Comptes rendus des séances de l'Académie des Sciences, Paris	68	101
	—	Annalen der Physik und Chemie, Poggendorf, Berlin	136	317 1069
1870	Hittorf	ditto	106	348
	Rundspaden	Quarterly Journal of Science, Crookes, London	7	138
1872	Blanc	Comptes rendus des séances de l'Académie des Sciences, Paris	75	537
1873	Becquerel	ditto	77	—
	Le Blanc	Transactions of the Chemical Society, London	26	242
1876	Gladstone	Journal of the Chemical Society, London	(1876)	152
1877	Berthelot	Annales de Chimie et physique, Paris	14	361
1878	Exner	Sitzungsberichte der naturwissenchaftlichen Klasse der kaiserlichen Akademie der Wissenschaften zu Wien	77	655
1879	Schoene	Journal of the Chemical Society, London	36	878

In the eightieth year of the previous century the technical application of the electrolysis of water was first taken up and we now come to the consideration of the real contents of the present publication.

II. THE CONSTANTS OF THE ELECTROLYTIC DECOMPOSITION OF WATER.

CHEMICAL AND ELECTROCHEMICAL CONSTANTS.

For the purpose of the easier comparison of the output of the processes to be described later, we will here collect together the chemical and electrochemical constants of the products of the electrolysis of water, *viz.*, of oxygen, hydrogen and detonating gas.

A. Oxygen.

Atomic weight = 16.
Molecular weight = 32.
Specific gravity = 1.10563 (air = 1).
1 liter at 0° C. and 760 mm. pressure = 1.43028 gram.
1 gram = 699 cubic centimeters.
1 coulomb sets free 0.0829 mg. = 0.058 cc.
1 ampere-hour sets free 0.298 gram = 208.8 cc.

B. HYDROGEN.

Atomic weight, 1.
Molecular weight, 2.
Specific gravity, 0.06926 (air = 1).
1 liter at 0° C. and 760 mm. pressure = 0.089578 gram.
1 gram = 11.1636 liters.
1 coulomb sets free 0.0104 mg. = 0.116 cc.
1 ampere-hour sets free 0.037 gram = 417.6 cc.

C. DETONATING GAS.

Specific gravity, 0.41468.
1 liter at 0° C. and 760 mm. pressure = 0.53614 gram.
1 gram = 1865 cc.
1 coulomb sets free 0.0933 mg. = 0.174 cc.
1 ampere-hour sets free 0.335 gram = 626.4 cc.

DECOMPOSITION VOLTAGE.

An approximate value for the voltage absorbed in the decomposition of water, sufficiently close for technical purposes can be obtained by Thomson's rule which starts from the assumption that the energy required for decomposition, that is, in our case, the electrical energy required must equal the heat of formation.

Since the heat of formation of water is 68,400 calories and 1 volt-coulomb = 4.18×10^7 ergs = 0.2394 cals, there is, therefore, required for the electrolysis of a gram-molecule of water

$$\frac{68{,}400}{0.2394} = 285{,}714 \text{ volt-coulombs.}$$

Since in the decomposition of the gram-molecule of water two gram-equivalents of hydrogen are set free at the cathode, which require, according to Faraday's law, 2 × 96540 coulombs, the decomposition voltage necessarily must be

$$\frac{285{,}714 \text{ volt-coulombs}}{2 \times 96{,}540 \text{ coulombs}} = 1.48 \text{ or roundly } 1.5 \text{ volts.}$$

The first theoretical investigations upon the electromotive force necessary to decompose water were made by Helmholtz,[1] who by different methods obtained for it 1.6447 and 1.783 volts. LeBlanc determined experimentally the decomposition point of water at 1.67 volts, at which electromotive force the

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[1] Ges. Abh., III, 92 and 267.

permanent passage of the current commences. Glaser repeated the investigations of LeBlanc in particular to clear up the contradiction that the H–O cell only gives 1.08 volts. Glaser found at this latter voltage a kink in the decomposition curve, but ascribed the same to the separation of doubly charged oxygen ions and explained hereby the contradiction with the gas cell. For further data, reference is made to the original work.[1] As the main results of a part of this work, Glaser promulgated the law that the decomposition of water, although it can take place primarily, in reality takes place mostly secondarily, especially with moderately strong currents.

CONDUCTIVITY.

The conductivity of water is, according to the work of Kohlrausch,[2] very small and is for pure distilled water in a column 1 m. long and 1 sq. mm. cross-section, at 18° C. 0.04×10^{-10} ($Hg = 1$).

For all practical purposes of electrolytic decomposition of water the latter must first be made conducting. For this purpose acids as well as bases are used. A table in the appendix gives data on resistances and conductivity of electrolytes used in the technical decomposition of water, that is, of sulphuric acid, caustic alkalies and the alkaline carbonates. M. U. Schoop[3] gives graphical representations of the connection between resistances of electrolytes and their concentration.

III. REVIEW OF THE PROCESSES.

Although it would be attractive and, in most respects, justifiable to describe the various apparatus and processes used in the electrolytic decomposition of water in a chronological order, yet the difficulty would arise in doing so, that apparatus of quite various principles would come close to-

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[1] Zeitschr. für Elektrochem., 1897–1898, 374. See also Caspari: Über Wasserstoffentwicklung, Zeitschr. für Elektrochem., 1899–1900, 37.

[2] Kohlrausch: Ztschr. phys. Chem., 1894, **14**, 317.

[3] Die industrielle Elektrolyse des Wassers, 1901, 113.

gether. By so doing, clearness of description would suffer.

We will, therefore, in the following pages, describe the processes by groups and give a chronological compilation at the close of this section in a tabular form.

The division into groups may most advantageously be made in the following way:

A. Processes and Apparatus for the Separate Production of Oxygen and Hydrogen.

- (a) *With Porous Diaphragms of Non-conducting Material.*
- (b) *With Complete Non-conducting Partitions.*
    - (*a*) For Instruction and Laboratory Work.
    - (*b*) For Technical Purposes.
- (c) *With Complete or Perforated Conducting Partitions.*

B. Processes and Apparatus for the Electrolysis of Water without Separation of the Gas (Production of Detonating Gas).

- (*a*) For Instruction and Laboratory Work.
- (*b*) For Technical Purposes.

C. Processes for the Simple Evolution of Oxygen.

- (a) *Through Depolarization at the Cathode.*
- (b) *By the Precipitation of Metal at the Cathode.*

A. Processes and Apparatus for the Separate Production of Oxygen and Hydrogen.

(a) With Porous Diaphragms of Non-conducting Material.

About the middle of 1880 the industrial application of the electrolytic decomposition of water began to be taken up and was commenced with the use of porous diaphragms.

Process of D'Arsonval, 1885.

In the years 1885-1887 d'Arsonval[1] used, in his medical lectures at the College of France, electrolytic apparatus for the manufacture of pure oxygen and applied the same in his researches upon respiration in closed spaces.

FORM OF APPARATUS.

The apparatus was for this purpose constructed of four similar decomposition cells made by Branville & Co., after the designs of d'Arsonval. As an anode, was used a perforated iron cylinder placed inside of a linen or woolen bag which served as a diaphragm. A 30 per cent solution of caustic potash was used as electrolyte. D'Arsonval observed no corrosion of the iron anode. The cathode consisted of a cylindrical vessel of sheet-iron 2 dcm in diameter and 6 dcm high. Each decomposition cell was intended for a current of about 60 amperes, from which the current density of not quite 2 amperes per sq. dm. of cathode surface may be calculated. D'Arsonval has given no data about the applied electromotive force.

The oxygen was collected and the hydrogen allowed to escape unused. The apparatus was in constant use for laboratory purposes only, and furnished per day 100–150 litres of oxygen, as required. The apparatus is said to have worked satisfactorily, except for the frequent renewal of the diaphragm.

D'Arsonval was about to describe his arrangement of apparatus at a meeting of the Physical Society of Paris in the beginning of 1888, when he heard of the somewhat better construction of Latchinoff's apparatus introduced about this time. Soon thereafter followed the work of Renard on the same subject. D'Arsonval had, therefore, to content himself with confirming the already published results, and by doing so illustrated the often observed fact that many experimenters, quite independently of each other, can arrive at similar results.

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[1] Elektrotech. Zeitschr. Uppenborn, 1891, 197. Grawinkl-Strecker: Hilfsbuch f. Elektrotech. Stohman-Kerl: Tech. Chemie, VII, 714.

Process of Latchinoff.

On the 20th of November, 1888, D. Latchinoff, of St. Petersburg, received the German patent 51,998,[1] for an "apparatus for the obtaining of hydrogen and oxygen by electrolysis."

PATENT CLAIM.

The patent claim runs:

"An arrangement of apparatus for the obtaining of hydrogen and oxygen on a large scale, by electrolytic decomposition of acid or slightly alkaline water, consisting in the combination of a direct current dynamo, one or more parallel connected batteries of decomposition cells with arrangements for the separate collection of the two evolved gases, drying apparatus for each of the two gases, as well as gasometers for the storing of the latter, and with the gas exits from the cells provided in such manner with floating valves, that the variations of pressure in the divisions of the cell automatically equalize themselves."

Latchinoff used either the iron electrodes with an alkaline electrolyte (10 per cent. solution caustic soda) like d'Arsonval or two carbon cathodes with one lead anode in 10–15 per cent. sulphuric acid.

FIRST METHOD OF OPERATION.

The arrangement of the apparatus is shown in Figs. 2 and 3[2]. The electrolyte is in a vessel made of stoneware, clay or glass, in which the level of the liquid can be observed in an external lip, *c*. A bell, *d*, serves for collecting the gas, and is provided with a flange, *f*, which rests on the edge of the outside vessel. The bell dips 6 cm. into the electrolyte and is divided into three sections corresponding to the three electrodes *a*, *b*, *a*. The tubes, *g* and *h*, lead to the gasometers.

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[1] Auszüge aus der Patentschrift, Patentblatt, II, 506, I. Chem. Centralblatt, 1890, II, 640. Chem. Ztg., 1890, 55, 906.

[2] La lumière électrique, 40, 234.

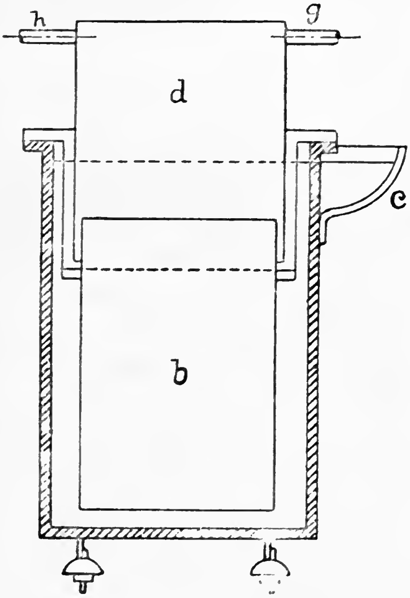

Fig. 2.

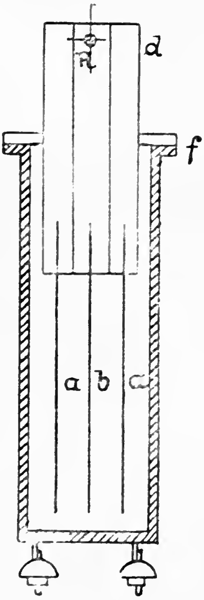

Fig. 3.

In order to prevent the mixing of hydrogen and oxygen in the electrolyte, two asbestos curtains stretched on a paraffined ebonite frame were hung between the electrodes, reaching down to the bottom of the stoneware vessel and up to the partitions of the gas bell.

Latchinoff carried on his investigations with electrodes 3 dm. wide and 5 dm. high, and used a current density of 14 amperes per sq. dm.

The single cells were placed in series and insulated from ground connections by three porcelain insulators which stood upon an asphalted plate.

LATER METHODS OF OPERATION.

The first practical form of the Latchinoff apparatus was found to be too easily broken when constructed on a larger scale. Latchinoff changed to another type of apparatus in which the outer vessel was made of metal and also served as the cathode.[1]

In Figs. 4 and 5, *a a* indicates a square vessel of cast- or wrought-iron. This is enlarged above and carries a bell, *d*, resting upon *f*. The vessel *a* is provided with an overflow, *e*, and is insulated by insulators and wooden stringers.

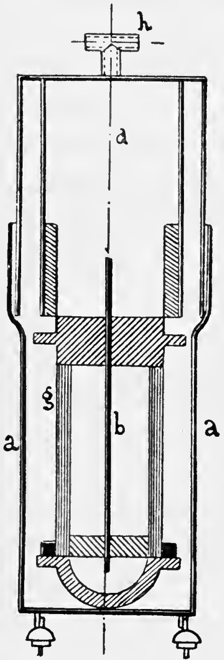

Fig. 4.

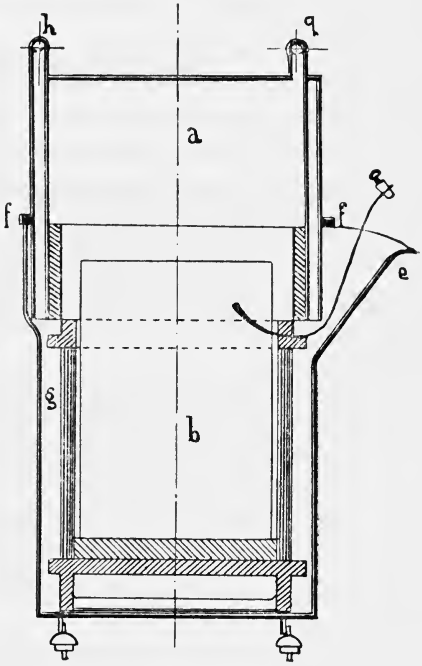

Fig. 5.

The cathode is formed by the vessel *a* itself while the piece of sheet-iron *b* serves as anode. The latter is surrounded by a box made of ebonite strips covered with parchment paper. The anode receives the current by an insulated wire introduced through the overflow underneath the lower edge of the bell. The bell *d*, likewise of iron, is divided into two spaces, which are in connection with the gas pipes by the T-joints, *g* and *h*.

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[1] Zeitschr. f. Elektrot., 1894, 338, 364 and 382. Electrochem. Zeitschr., 1894–95, 106.

Since the bell *d* is in electrical connection with the cathode vessel, the lower part of the inner chamber of *d* is lined with hard rubber above the level of the liquid, in order not to contaminate the oxygen passing into it, by hydrogen which might be thereupon developed. In the apparatus the electrolyte was also a 10–15 per cent. solution of caustic soda as free as possible from carbonates.

The apparatus containing not quite 60 litres required 300 amperes. The anode measured 9x5 dm. and had therefore on both sides 90 sq. dm. surface. The outer vessel measured 50x100x11 cm. The current density at the anode was therefore 3.5 amperes per sq. dm. The single cells were connected up as shown in Fig. 6.

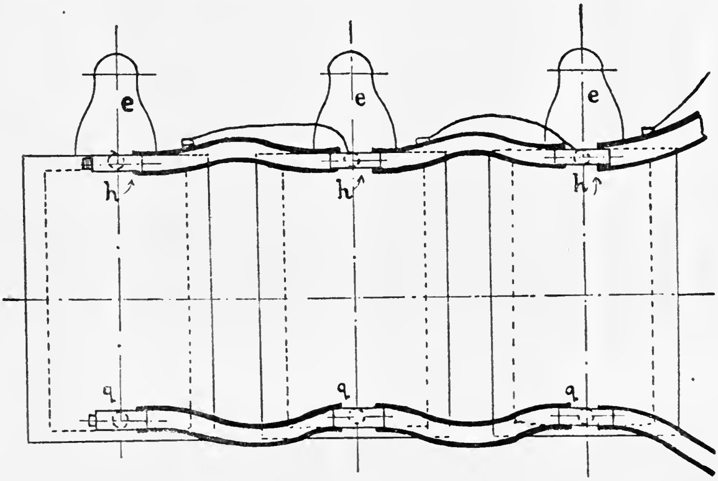

Fig. 6.

The gases were collected by a series of pipes with connections to each apparatus, and dried before going to the gasometer.

DRYING OF THE GASES.

For a drying chamber a long box with rounded cover was used, with a partition reaching not quite to the bottom, and on both sides of the partition lay a quantity of pumice stone soaked with sulphuric acid. The gases entering into one side of the partition were forced to pass through the pumice, under the partition, and up on the other side. The gases are therefore not only dried but also freed from any particles of alkaline electrolyte carried out with them.

MODERATION OF COMPLICATIONS.

To avoid irregularities in the electrical decomposition, mercury manometers are provided which are connected with one pole of an alarm bell. The second pole of the alarm bell was connected to a platinum wire sealed into the upper part of the manometer tube. When the pressure rises in the apparatus the mercury is forced up the tube of the manometer and when it reaches the platinum wire mentioned, completes the circuit and rings the bell.

BIPOLAR CONNECTIONS.

Latchinoff was the first to use bipolar electrodes in the electrolytic decomposition of water. For smaller plants as in laboratories, pharmacies, etc., a long box about 2 metres long made of paraffined wood is divided by air-tight electrode plates into a series of chambers. Between the electrodes were placed diaphragms of parchment. All the intermediate partitions acted as double plates since only the two external ones were connected with the source of the electric current. An apparatus with about 40 electrodes could therefore be connected directly to a normal lighting circuit. Latchinoff used a current density of about 10 amperes per sq. dm. of electrode surface for such an apparatus.

Dr. O. Schmidt, as we shall see later, has used recently this principle of bipolar arrangement of electrodes in a practical apparatus, but Latchinoff was the first to propose it for the decomposition of water.

ELECTROLYSIS UNDER PRESSURE.

Likewise Latchinoff was the first to propose and carry out in a decomposition apparatus the compression of the gases.

Proceeding from the assumption that even considerable pressure would be without influence upon the output, he arranged the apparatus so that it was connected directly with a steel tube intended to stand a gas pressure of 100-120 atmospheres.

The apparatus shown in Fig. 7 consists of a cylindrical steel vessel which is closed by a cover tightly screwed on. The tubular iron electrode *b* in the middle of the tube is raised upon an insulating stand, *g*. It is connected with the binding post *f* by an insulated wire, *k*. The second binding post *f'* is directly screwed into the steel cylinder, which forms the second pole.

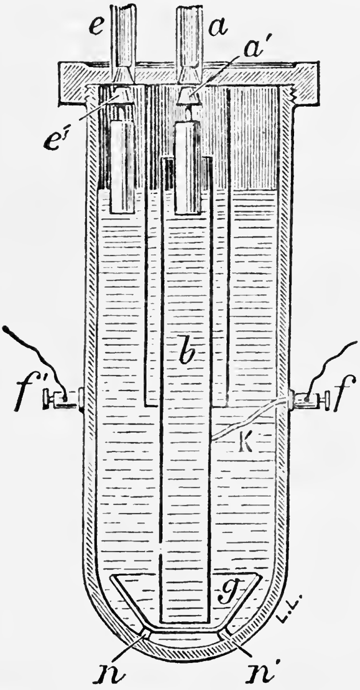

Fig 7 ..

The cover carries two pipe connections, one in the middle and the second on one side. At the lower edge of the tubes is a conical valve, supported upon a cylindrical float, which latter works on a guiding tube not shown in the drawing. An insulated cylinder, whose lower part dips into the electrolyte, serves to prevent the mixing of the gases. The insulating stand *g*, with its flaring sides opening upwards, serves to direct any gas evolving from the bottom of the steel cylinder towards the sides of this cylinder, so that it rises into the outer space at the top.

The apparatus is filled three-fourths full of caustic soda solution. The tube connections *e* and *a* are joined with the steel cylinder in which the gases are to be compressed. The oxygen reservoir must only be one-half as large as the hydrogen reservoir in order that the gas pressure remains the same. It is, however, impossible to avoid small variations in pressure which would lower the level of the liquid in one of the electrode spaces, and thereby give opportunity for the formation of detonating gas.

This danger is avoided by the use of the floating valves *a′ e′*. As soon as the level of the liquid rises higher in one of the compartments the valve, as for instance *a′*, rises with the rising electrolyte and closes the gas exit, whereupon the gas, being still evolved, reduces the level. As soon as the valve is no longer held in place by the float it falls back and allows the gas in question to pass out. This provides an automatic regulator to the pressure.

Unfortunately, there is in the literature of the subject no information as to whether this apparatus was tried on a large scale, and whether or in what manner the increasing absorption of the gases in the electrolyte by increased pressure made itself noticeable.

PLANT.

Latchinoff gives the following figures for an industrial plant[1]:

A 50 H. P. source of energy drives a direct current dynamo furnishing 300 amperes and 110 volts. The electrolytic plant consists of 44 baths, each one 1.4 metres high, and requires 5x1½ metres of floor space. The number of cells therein mentioned in the journals, namely, 40 in series, must be a mistake, since in this case the production named would be theoretically scarcely possible. Latchinoff used 44 cells which number he also mentions in another place as using with a 100 H. P. plant and 110 volts working tension.

A 50 H. P. plant produces, per hour, 5.5 cubic metres of hydrogen and 2.75 cubic metres of oxygen or together 8.25 cubic metres of gas, or 100 cubic metres of oxygen and 200 cubic metres of hydrogen in thirty-six hours, decomposing 150 litres of water.

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[1] Elektrochemische Zeitschr., 1894–95, 108.

OUTPUT.

The theoretically possible output would be 626.4 × 300 × 44 × 36 = 297.6 cubic metres of gas. Latchinoff has, therefore, assumed a theoretical current output and has reckoned out with reference to the chosen voltage used an energy output of 57.6 per cent.

COST OF OPERATION.

Latchinoff has also given estimations of the working cost of his process. In order to be able to compare the calculated cost of production, we will assume always two extreme cases, namely, when power costs on the one hand ¼ cent per kilowatt-hour for water power, and on the other hand 1¼ cents for steam power in small plants. The data of Latchinoff would then reckon up for the manufacture of 100 cubic metres of oxygen and 200 cubic metres of hydrogen in thirty-six hours as follows:

1188 kilowatt hours..........	$2.97	$14.85
Caustic soda................	0.08	0.08
Drying of gases.............	0.24	0.24
Attendance	4.05	4.05
Total.................	7.34	19.22

Therefore, according as to whether only the oxygen, or only the hydrogen, or both gases are assumed as salable, we make these calculations:

a. With water power,	1 cubic metre of oxygen costs	7.34 cents.
	1 cubic metre of hydrogen costs	3.67 cents.
	1 cubic metre of detonating gas costs	2.45 cents.
b. With steam-power,	1 cubic metre of oxygen costs	19.22 cents.
	1 cubic metre of hydrogen costs	9.61 cents.
	1 cubic metre of detonating gas costs	6.40 cents.

Sinking fund and interest on the capital invested are not included in these figures.

PRACTICE.

It is not known whether plants after Latchinoff's methods have been industrially operated. The apparatus is said to have been publicly exhibited in the IV Electrotechnical

Exposition, opened the 24th of January, 1892,[1] at St. Petersburg. The baths were, however, injured by an accident at the exposition, so that instead of being in continual operation, as was intended, they were only operated a short time.

Several French investigators were working on the problem of the technical electrolysis of water simultaneously with Latchinoff, and, according to all appearances, independent of him.

Process of Ducretet, 1888.

Ducretet, for instance, constructed many forms of apparatus for the decomposition of water, using alkaline electrolytes.

FORM OF APPARATUS.

One of these forms of apparatus is shown in Fig. 8. The iron cylinder E′ serves at the same time as an electrode and container for the electrolyte. The bottom *i* is covered with an insulating layer and bears the supply tube T′. The cover Co is insulated and is screwed on the tube. One of the connections, *e*, is united with a centrally placed cylinder made of iron wire netting, which forms the second electrode. The cylindrical asbestos diaphragm S S divides the tube into an anode and a cathode space, and the gases escape at T′ and G′.[2]

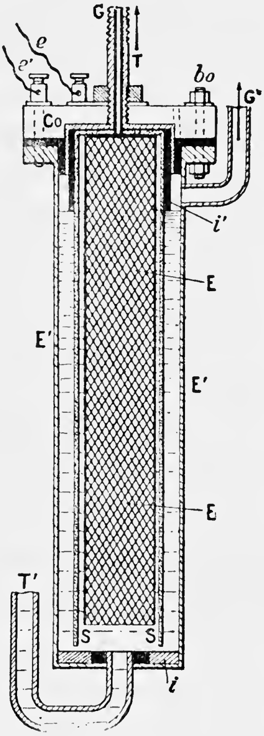

Fig. 8.

Process of Renard, 1888 to 1890.

The construction of Renard rests on a similar principle. He began his work in electrolytic decomposition in 1888 and communicated his results obtained in a séance of the

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[1] Chem. Ztg., 1892, 28, 461. Elektrochemische Zeitschr. 1894–95, 106.

[2] La lumière électrique, 40, 234.

French Physical Society, December 5, 1890. Renard took up the question primarily as commander of the balloon corps at Chalais, and, in consequence of this, had in view a simple and cheap method of obtaining hydrogen for the filling of balloons.

OUTPUT.

Renard gives the following output as obtained in a practical application of his apparatus.[1]

Volume of hydrogen at 10°C and 760 mm.	0.433 litre, per ampere-hour.
" " " " "	0.144 litre, per watt-hour.
Ampere-hours consumed per cubic metre of hydrogen,	2310.
Watt-hours " " " " "	6930.
H. P. hours " " " " "	9.4

Renard assumed, therefore, nearly a theoretical current output, and at a working voltage of 3 volts, a useful energy effect of about 50 per cent.

He worked on the theory that the platinum used in the laboratory apparatus for the decomposition of water may be replaced by a cheaper material, and, besides that, he tried to find a diaphragm which would separate the gases without introducing too much resistance.

In consequence of these endeavors, he replaced acid electrolytes by alkaline solutions and hereby was enabled to use cast-iron or steel as electrode materials. Since clay diaphragms showed too high a resistance for the purpose in view, Renard used asbestos as a diaphragm material, its resistance being practically negligible.

As an electrolyte, he used a 13 per cent. solution of caustic soda, the resistance of which is the same as that of a 27 per cent. solution of sulphuric acid.

FORM OF APPARATUS.

The simplest construction used at Chalais consisted of a large cylindrical sheet-iron vessel, which acted simultaneously as cathode and a container for the electrolyte. A perforated sheet-iron cylinder which hung from the insulated cover of

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[1] La lumière électrique, **39**, 39.

the vessel, served as anode. An asbestos sack drawn over this served as a diaphragm.

This consists of exactly the same principle of construction as was seen in the apparatus of Ducretet.

Renard showed to the French Physical Society two types of apparatus, one weighing 2 kg., using a current of 25 amperes at 2.7 volts, while the second was intended for a current of 365 amperes at 2.7 volts, and furnished 158 litres of hydrogen per hour. The price of an apparatus of this latter size was given as $20.

PRACTICE.

Such an apparatus was in operation at Chalais for six months, and at the end of this time both electrodes and diaphragms were in the best of condition.

According to the report of Renard the hydrogen obtained was pure and the oxygen free from ozone in consequence of the alkaline solution, so that the use of rubber for connections was permissible. The gases were washed with tartaric acid in order to remove the spray of the alkaline solutions.

COST OF PLANT AND OPERATION.

The cost of a plant which used 36 of the larger-sized electrolyzers, and furnished 5.7 cubic metres of hydrogen and 2.85 cubic metres of oxygen per hour (= 136 cubic metres of hydrogen and 68 cubic metres of oxygen per 24 hours), was estimated by Renard to be $8100 and the cost of operation, including the compression of the gas to 120 atmospheres, 10 to 12 cents per cubic metre of hydrogen. It was assumed in these figures that $2^1/_5$ pounds of coal would be used per H. P. hour in generating current.

LABORATORY APPARATUS.

Besides the apparatus for the technical manufacture of hydrogen for the filling of balloons, Renard constructed also larger laboratory apparatus which were then furnished by Ducretet in Paris[1].

[1] La lumière électrique, **43**, 432.

These apparatus were very similar to the above-described Ducretet apparatus and are shown in Fig. 9.

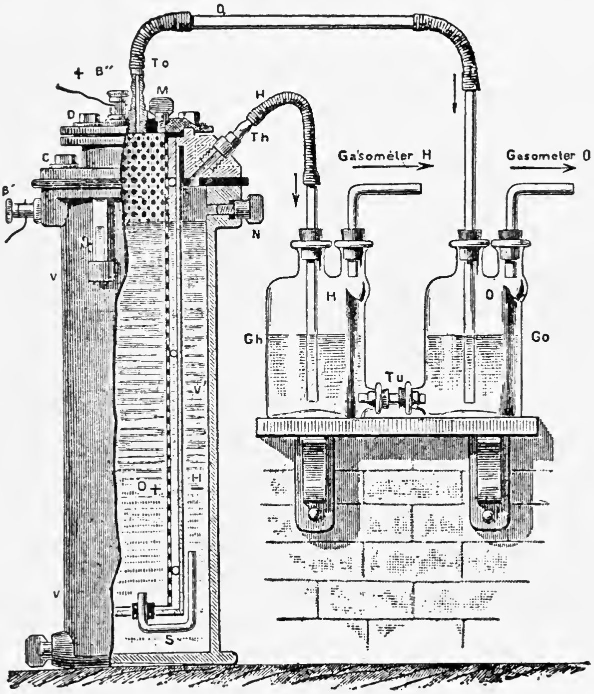

Fig. 9.

This laboratory model measured 40 cm. high, 18 cm. diameter, and could take a current of 60 amperes using 4.5 volts. The production was 26 litres of hydrogen and 13 litres of oxygen per hour. With a normal tension of three volts the apparatus passed 25 amperes, producing 11 litres of hydrogen and 5.5 litres of oxygen per hour. The materials used and the electrodes were the same as in the formerly described apparatus of Ducretet. Instead of asbestos diaphragms clay cylinders were used, in order to obtain very pure gases. In this case the cylinders are perforated at the bottom and contained a bent tube, S, which connected the two electrode chambers.

The electrolyte was poured in at M. The two gas bottles

G*h* and G*o* served to equalize the differences of pressure, a n contained a 5 per cent solution of tartaric acid to absorb the alkaline spray carried over. As the current density increased, the voltage used and the output increased in the following manner:

TABLE II.

Amperes.	Volts.	Litres hydrogen per hour.	Litres oxygen per hour.	Temperature.
2	2.06	0.87	0.43	25.5°
5	2.24	2.16	1.08	
10	2.41	4.33	2.16	
20	2.84	8.66	4.33	
25	3.04	10.82	5.41	
40	3.65	17.32	8.66	
50	4.00	21.65	10.82	
60	4.40	26.00	13.00	

Process of Delmard, 1890.

The principle of construction as used by Ducretet and Renard was patented in Germany by Delmard in the German patent 58,282 of November 23, 1890.

The patent claim embraces:

1. "An electrolytic apparatus for the decomposition of water consisting of an iron vessel, *g*, in which an iron tube, *h*, provided with perforations, *o*, and surrounded by a sack of asbestos cloth, is hung from the cover *l*, and insulated therefrom, said cover being provided with two pipe connections for the taking off of the hydrogen and oxygen, and so arranged that the outer vessel forms the + and the inner tube *h* the — electrode." (See Fig. 10.)

2. " In combination with the apparatus described under 1, a pressure regulator consisting of the vessels A and B connected by a tube, T, close to their bases, into which vessels the hydrogen and oxygen coming from the generator are led by the tubes O and H, which dip to the same level in the two vessels, atmospheric air being excluded." (See Fig. 11.)

It is not necessary to further describe these patent specifications since they furnish nothing new compared to Ducretet and Renard. The apparatus is merely as compared with these latter considerably longer.

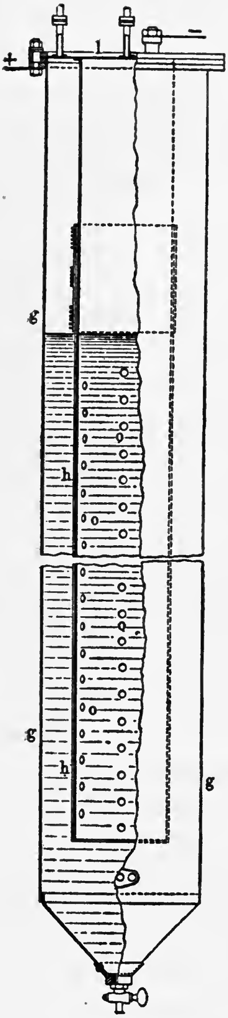

Fig. 10.

It is quite probable that this patent is only a German patent application of Renard's under a strange name.

Nothing is known of any industrial application of this type of apparatus, especially in Germany.

Process of Bell, 1893.

We first find something new in apparatus for the decomposition of water, using porous diaphragms in the German patent 78,146 of October 30, 1893, describing the apparatus of Bell.[1]

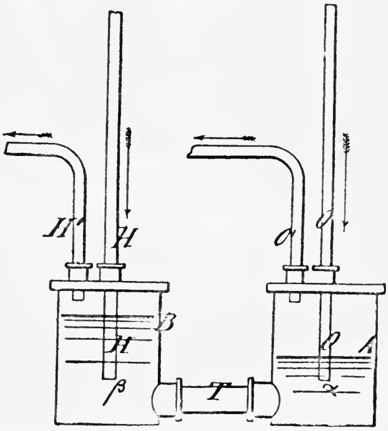

Fig. 11.

PATENT CLAIM.

Patent claim :

"An arrangement for the continuous charging of apparatus for the electrolytic decomposition of fluids, in which the electrodes are separated from each other by a partition, consisting therein, that these partitions themselves, or an extension of

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[1] Extracts in Zeitschr. Elektrochem., 1894-95, 429. Jahrbuch f. Elektrochemie, 1895, 193. Ahrens: Handbuch der Elektrochemie, 1896.

the same made of capillary netting or a similar material, have their upper edge turned over and dipping into the vessel *g g* above the decomposition space and filled with an electrolyte or another suitable fluid by a funnel, *i*, and out of which the electrolyte or other fluid is sucked up, and by the proper regulation of the level of the fluid in the vessel *g g* furnishes to the electrodes, by the principle of capillarity and gravity, a fresh quantity of fluid as the latter is decomposed."

FORM OF APPARATUS.

The apparatus, as shown in Fig. 12, contains on a base

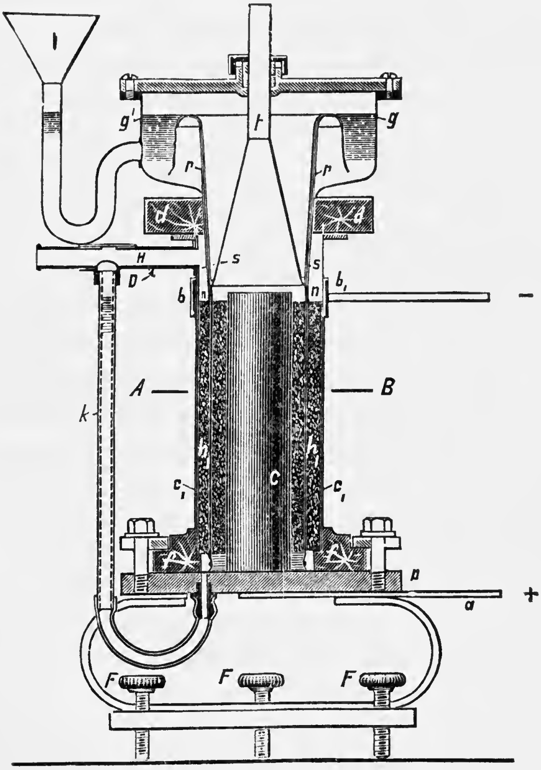

Fig. 12.

plate, *p*, two concentric hollow cylinders, c_1 and c_1, of cast-iron, which are described in the patent specifications as being of circular section. Both cylinders are insulated from each other by a non-conducting clamp, *f*, and covered by an insulated cover, *d*. The funnel *g* passes through the middle of the cover which contains an inverted conical tube, *r*. An asbestos web, *s*, in which is interwoven vertical vegetable fibres of linen or wool, hangs between the electrodes. The lower end of the cylindrical diaphragm is fastened to the hard rubber clamp surrounding the one electrode holder, while the upper end is turned over the tube *r*. The funnel-shaped vessel *g* is covered with an air-tight cover, in the center of which a funnel-shaped tube, *t*, is fastened by means of a stopper, and reaches down almost to the upper end of the electrode *C*. The outer containing vessel *C* carries the nipple *D*, on the end of which, as well as on the end of the tube *t*, the rubber tubes serving to carry off the gases may be slipped. A copper band, *b*, which surrounds the outside hollow cylinder, takes the current to the negative pole, while the positive conductor is connected to the inner cylindrical electrode by means of the plate *a*, in contact with the base plate *p*. The spaces between the electrodes and the diaphragm were filled to *n* with pieces of cast-iron or some other broken conducting material which is not attacked by the electrolyte. This makes a coherent conducting layer which reaches to the diaphragm.

This direct contact of the electrodes with the diaphragm is obtained by Bell by still other arrangements, such as by two narrow spirals of steel wire upon which the asbestos mantel is clamped. In this case the inner cylinder can be completely omitted while the outer cylinder serves as a container. In this the fundamental condition is always that the gases evolved must be able to escape easily.

The electrolyte is poured in through the siphon-shaped funnel *i* connected with *g*. A 15 per cent. solution of caustic soda is used for electrolyte. The electrolyte is run in until it flows over the edge of *r* and runs down the asbestos mantel into the apparatus. After that the asbestos mantel absorbs the electrolyte constantly by capillary action. The height of the electrolyte can be observed in the tube h_1.

Fig. 13 shows a cross-section through the two electrodes and the diaphragm, while Fig. 14 shows another arrangement which gives to the diaphragm and therefore also to the electrode surfaces a greater area.

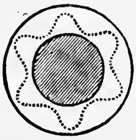
Fig. 13.

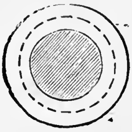
Fig. 14.

Although the thought of obtaining the greatest possible electrode surface by this filling with metallic granules is quite reasonable, yet we must not leave out of consideration that the electrodes may be coated over by impurities which separate out during electrolysis, and thereby produce difficulties in the operation.

PRACTICE.

It is not known that this apparatus has gone into practical use. The whole construction reminds one more of a simple laboratory research, as seems particularly indicated by the three set-screws *F* which are only used upon instruments requiring fine adjustment. These are for the purpose of making an exact horizontal adjustment of the edge of the diaphragm above *r*.

After the above-described attempts of Bell, practical electrochemists, who worked on the electrolytic decomposition of water, turned to other principles of construction which will be described in the latter part of this work, while the use of porous diaphragms fell more into the background.

Process of Schmidt, 1899.

It was not until the year 1889 that Dr. O. Schmidt returned to the use of porous diaphragms and obtained a patent for the apparatus described in the German patent 111,131, June 13, 1899.[1]

PATENT CLAIM.

Patent claim:

"An apparatus for the electrolysis of water consisting of many series of plates after the fashion of a filter press, and characterized by having the pipes for conducting off the gases communicating with the water supply pipes, for the purpose of taking back into the electrode compartments the water carried out by the gases."

DESCRIPTION.

The fundamental idea of the Schmidt invention consists, therefore, in an apparatus with numerous cells placed like a filter-press and characterized by the fact that the current communicated to the water in the direction of the gas exits, by the evolution of the gas, causing a large outflow of water, is converted into a rapidly circulating system. This is obtained by making the gas exit pipes connect with a vessel called the gas separator which connects with the pipes furnishing the cells with water. Since the water carried out by the gases is thus returned to the electrolyte in the cells, very little loss of electrolyte ensues.

The apparatus is shown in one example in Figs. 15–18, in the form in which the electrodes are connected in series.

Fig. 15 shows the apparatus in side elevation, Fig. 16 in horizontal section, Fig. 17 a front view of one of the frames as seen from the anode side, and Fig. 18 is a vertical middle section through the gas separator *O* for the oxygen. *e*, *e* are the double pole electrodes touching each other at the thick edges, and *d* the diaphragms placed in between the electrodes to produce the electrode spaces and simultaneously insulate the edges of the electrodes from each other.

Each plate, *e*, has at top and bottom, in its thick edges, two

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[1] Descriptions in Zeitschr. Elektrochemie, 1900–01, 294. Elektrochem. Zeitschr., 1900–'01, 230.

bore-holes h o and w w^1 (Fig. 17), so that the apparatus is penetrated above and below by two channels, the lower one serving to supply the electrode spaces with water and the upper

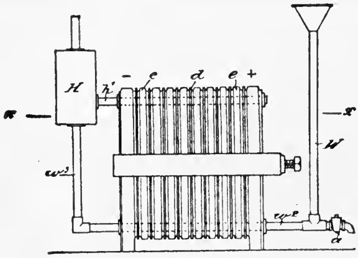

Fig. 15.

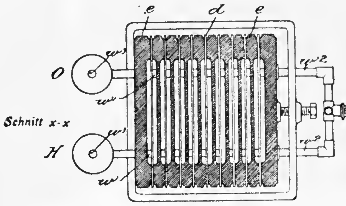

Fig. 16.

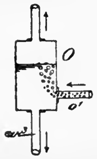

Fig. 18.

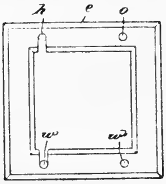

Fig. 17.

for the leading-off of the evolved gases, since w and h are each connected with the cathode spaces and w^1 and o each with the anode spaces.

The two water channels w and w^1 at one end of the apparatus communicate by the tube w^2 w^2 with a common water escape W, and at the opposite end the two gas channels h and o are each in connection with the gas separators for hydrogen and oxygen through the tubes h^1 and o^1 (the latter covered by the former in Fig. 15). Regarding the two gas separators, H communicates by the down-take tube w^3 with the water channels w and o, and moreover, likewise communicates with the water channel w^1 at this end. The gas separator consists of a vertical cylindrical vessel with a gas exit in its cover; the inflow of water through *W* is so controlled that the gas separator is filled with water above the entrance of the gas tube. The gases ascend into the gas separator carrying with them their water spray, leaving the latter in this vessel. At the same time the water flows out of the gas separator through the down-take tube into the connecting water channels. The branch connection *a* serves for emptying the apparatus.

Schmidt has therefore taken up the bipolar arrangement for electrolytic decomposition of water as proposed by Latchinoff, and made it technically applicable by the filter-press-like construction. This construction gives also the advantage of a small floor space as well as economy in insulation, wire connections and gas exit tubing.

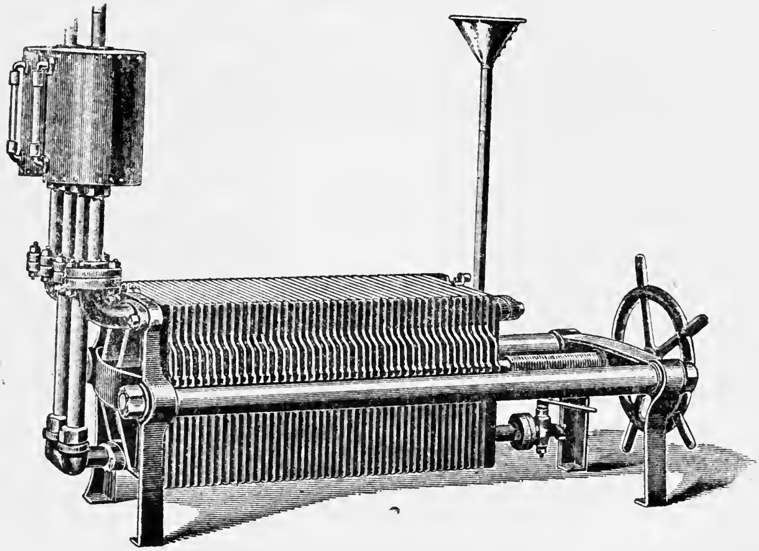

Fig. 19.

A perspective view of a Schmidt electrolyzer is shown in Fig. 19.

FORM OF APPARATUS.

In the apparatus, Schmidt uses asbestos cloth for diaphragms, reinforced with rubber on the edges for the purpose

TABLE IV. FOR 110 VOLTS.

Number of chambers.	Distinction.	Amperes.	Kilowatts.	Litres per hour.		Cubic metres per twenty-four hours.		Approximate capacity in litres.	Diameter of supply pipes in inches.	Weight in kilograms.
				H	O	H	O			
44	B 15	15	1.65	275	137	6.6	3.3	100	¾	700
	B 30	30	3.30	550	275	13.2	6.6	200	1	2500
	B 60	60	6.60	1100	550	26.4	13.2	500	1¼	4200
	B 100	100	11.00	1850	925	44.4	22.2	800	1½	7500
	B 150	150	16.50	2750	1375	66.0	33.0	1200	1¾	14000

ARRANGEMENT.

Fig. 20 shows the arrangement of the Schmidt plant. The main conductors pass over a small switchboard provided with lead fuses, ampere metre, and a small regulating rheostat which may be switched in and out of the circuit. The contents of the apparatus may be let out in a basin into which the distilled water needed for refilling is also introduced. The filling and supplying are provided for by a small hand-pump.

Pressure gauges are provided on the gas-conducting pipes before they branch off into the gasometers.

RULES FOR OPERATING.

Schmidt has given out a series of articles upon the construction and operation of his apparatus which are here reproduced, because, with the exception of the after data relating to the special construction of his apparatus, they will serve as general information for the other processes for the electrolytic decomposition of water.

(*a*) GASOMETER.

The gasometers should never be set up in the same room in which the persons work or which is used as a thoroughfare by the employees, and are always to be erected in an open space which is at a considerable distance from occupied rooms and work places.

It is best for the gasometers to stand entirely isolated, and access to trespassers prevented by a suitable fence.

at Bochum, 99.8 per cent. oxygen, 0.1 per cent. carbonic acid and 0.1 per cent. nitrogen.[1]

TYPES OF APPARATUS.

Schmidt builds two series of apparatus types for better adaptation to existing lighting circuits with direct current, *i. e.*, for the usual tensions of 65 and 110 volts.

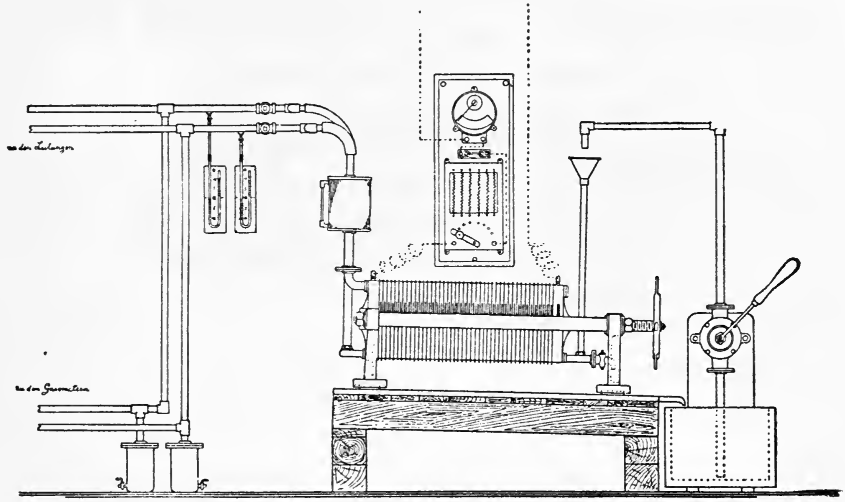

Fig. 20.

The normal sizes of such apparatus are given in tables III and IV:

TABLE III. FOR 65 VOLTS.

Number of chambers.	Distinction.	Amperes.	Kilowatts.	Litres per hour.		Cubic metres per twenty-four hours.		Approximate capacity in litres.	Diameter of supply pipes in inches.	Weight in kilograms.
				H	O	H	O			
26	B 15	15	0.975	163	81	3.90	1.95	60	¾	500
	B 30	30	1.950	325	162	7.82	3.91	120	1	1750
	B 60	60	3.900	650	325	15.64	7.82	250	1¼	2700
	B 100	100	6.500	1085	542	25 92	12.96	400	1½	5300
	B 150	150	9.750	1630	815	39.10	19.55	750	1¾	10000

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[1] Private communication to the author.

TABLE IV. FOR 110 VOLTS.

Number of chambers.	Distinction.	Amperes.	Kilowatts.	Litres per hour.		Cubic metres per twenty-four hours.		Approximate capacity in litres.	Diameter of supply pipes in inches.	Weight in kilograms.
				H	O	H	O			
44	B 15	15	1.65	275	137	6.6	3.3	100	¾	700
	B 30	30	3.30	550	275	13.2	6.6	200	1	2500
	B 60	60	6.60	1100	550	26.4	13.2	500	1¼	4200
	B 100	100	11.00	1850	925	44.4	22.2	800	1½	7500
	B 150	150	16.50	2750	1375	66.0	33.0	1200	1¾	14000

ARRANGEMENT.

Fig. 20 shows the arrangement of the Schmidt plant. The main conductors pass over a small switchboard provided with lead fuses, ampere metre, and a small regulating rheostat which may be switched in and out of the circuit. The contents of the apparatus may be let out in a basin into which the distilled water needed for refilling is also introduced. The filling and supplying are provided for by a small hand-pump.

Pressure gauges are provided on the gas-conducting pipes before they branch off into the gasometers.

RULES FOR OPERATING.

Schmidt has given out a series of articles upon the construction and operation of his apparatus which are here reproduced, because, with the exception of the after data relating to the special construction of his apparatus, they will serve as general information for the other processes for the electrolytic decomposition of water.

(*a*) GASOMETER.

The gasometers should never be set up in the same room in which the persons work or which is used as a thoroughfare by the employees, and are always to be erected in an open space which is at a considerable distance from occupied rooms and work places.

It is best for the gasometers to stand entirely isolated, and access to trespassers prevented by a suitable fence.

In locations in which strong winds or frost are to be expected the gasometers must be under cover, which latter must be constructed as light as possible and is best covered with roofing paper. The side walls of the building may be built of masonry.

No stones, pieces of metal or other solid bodies must be used for weighing down the holders. It is much more to be recommended to load up the bell by the use of fine gravel or water.

The gasometers are to be so arranged that the bells, in order that they may be completely emptied, can sink entirely into the basin.

(*b*) CONDUCTORS AND WATER SUPPLY.

The supply pipes may be iron or lead tubes. The latter metal must always be used where corrosion of the pipes by moisture, acids or other vapors is to be feared.

The conductors may be carried on the walls of the buildings like gas pipes, through the air, or let into the ground, yet care must be taken that the lowest points are provided with sinks, having drainage coils for the purpose of removing condensed water.

A very careful fitting of the same is necessary on account of the small weight and great capacity of the hydrogen for diffusion.

The arrangement of the conducting pipes is under all conditions to be such, that two systems of piping lead from the gas-generating plant directly to the gasometers. The branch pipes for leading off the gases to where they are used is to be connected to these conductors at only *one place* in each.

Just back of the branching off a water seal must be placed, such as a water-bottle, in order to prevent any ignition of the gas in the distributing pipes by a communication backwards to the contents of the gasometer.

These water seals prevent, also, the escape of the gas from one gasometer into the other if by carelessness a connection has been left between the distributing pipes, and the pressure in the two gasometers may be unequal.

(*c*) MEASURING AND CONTROLLING APPARATUS.

Just back of the connections of the generator to the conductors leading off the gas to the gasometers, cocks must be placed.

(*a*) *The pressure guage.* This consists of a U-shaped, bent glass tube which is half filled with colored water and has a millimeter scale attached.

Care must be exercised that the pressure in the two side conducting pipes is always kept the same.

(*b*) *The controlling apparatus.*—This consists of two small, thin glass, water-bottles with metal bases. The exit points are of metal with a wide bore; they stand very nearly opposite to each other. A small quantity of gas escapes constantly from them, which is kept ignited.

If a mixture of gas enters them, the contents of the flask ignite instantly and the demolition of them gives notice at once of the dangerous condition existing.

(*d*) COCKS AND JOINTS.

The cocks used should be only of the best material (bronze) and very carefully ground in.

It is a particular characteristic of pure oxygen that when in a moist condition it attacks metals much stronger and quicker than air, and the cocks must, therefore, be tested more frequently as to their condition than otherwise necessary.

All joints are to be made carefully with asbestos, avoiding rubber and other combustible substances.

(*e*) GAS PRESSURE.

The gas pressure can be chosen according to the wished-for purposes, but care must be taken that it is sufficiently high to overcome the back pressure in the water seals.

The advice to keep the pressure equal in both conductors is only necessarily observed when both gases are utilized.

If one gas is left to escape, the pressure in this conductor is kept somewhat smaller to insure greater security.

(*f*) BURNER.

Although it is possible to lead both gases through a hose to the blowpipe, by using an ordinary T connection provided with cocks, yet there is in such apparatus some certain danger of the flame striking back, which may be caused by a kinking of the hose or by some one carelessly treading upon the tube.

It is therefore recommended to use only such blowpipes in which both gases are brought to the mixing point in separate pipes, and these connected with the point of the branch pipe by a reinforced tube.

To avoid with certainty the striking back of the flame it is necessary that the current of gas have a certain minimum velocity in the point of the burner. Since the gas pressure is constant, the burner point must have different-sized openings according to the sizes of the flame to be used.

The introduction of tubes with wire mesh partitions is not a sure protection, since the wire gauge is in many cases traversed by the flame.

The gas pressure is so chosen that it is large enough for the largest-sized burners. With a blowpipe point of 1 mm. diameter the gas pressure must be at least 200 mm. of water.

The starting of the burner must always be done by first turning on the hydrogen cock and igniting the gas ; only then is the oxygen cock to be opened with care, until the required mixture has been obtained. In putting out the flame a reverse order is to be followed—oxygen is first turned off and afterwards the hydrogen, otherwise the flame is very apt to strike back. Mixing cocks are very much to be preferred which possess a plug with double boring, moved by a spring, by which the opening up and shutting off of the gases must take place in the right order.

(*g*) SETTING UP OF THE APPARATUS.

In setting up the apparatus special care must be taken that the passages are carefully cleaned out and do not contain foreign matter.

The diaphragms must be put in place with particular care so that the sides provided with rubber are towards the negative electrode surfaces, at which the hydrogen gas is evolved. Care must also be taken that no moving of the holes from the perforations in the plates takes place, which would result in narrowing the passages.

The work of setting up can be made easier by loosely screwing up the lugs and passing through them a suitable rod.

The apparatus must be well insulated from the earth and also have no metallic connections with the gas pipes; tests must be made to see that the insulation in the apparatus itself is in good condition.

(*h*) CHARGING.

The charge of the apparatus is a 10 per cent. solution of pure refined potassium carbonate (pearl ash) in distilled water, of specific gravity 1.100. It must contain no appreciable amount of mineral acids or chlorine.

(*i*) STARTING UP.

Before the apparatus is filled and closed, the gas pipes, gasometers and the cocks are to be tested for their tightness in the usual manner. The gasometers must be quite empty.

After the apparatus has been filled it should work for a short time with the pipes branching from the gas pipes open, and connection with the gas pipes only made when the solution has stopped foaming or the latter has moderated greatly.

Care must be taken that no great difference of pressure arises in the two gas conductors.

After tests have been made on the escaping gases and their purity has been proven, the gasometers may be connected up and commence to be filled. (The purity of the gas is best tested by leading a little of it through a rubber tube into a test-tube entirely filled with water and when the latter is filled with gas, close the end with the thumb, and bring it near a flame. The hydrogen should burn quietly and the oxygen should not ignite.)

(*k*) OPERATION.

The height of the liquid in the gas separators must always be kept in view since it is absolutely necessary that the chambers of the electrolyzer be always filled with the fluid and the collection of gas in them prevented.

The apparatus decomposes 134 cubic centimetres of water per kilowatt hour and this quantity must be replaced.

The replacement must be done by means of distilled water. Should the solution foam very strongly at the start, some petroleum can be poured into the gas separator.

The apparatus must be taken apart every four weeks and cleaned; the electrolyte can be used over.

If the apparatus takes too much or too little current, the voltage between the single plates or electrodes is to be tested by a voltmeter. If the chamber shows no tension, or only very little, it indicates that a short circuit has taken place through the metallic portions of the two electrodes; if the tension is extremely high, it indicates a complete or partial emptying of the chambers by reason of the stopping up of the exit channels.

In both cases the apparatus must be taken apart and given a thorough cleaning.

It is recommended that the apparatus be cut out of the circuit as seldom as possible; at times of small gas requirement, and over night, it is left working, when practicable, with a quite small current.

If after long use of the apparatus it appears that some of the electrode surfaces at which the oxygen is being evolved show a strong oxide covering, and the chambers will let through no more current, the condition may be remedied by changing the poles of the apparatus. This operation is to be done only with the greatest care, and the apparatus is not to be connected to the reversed conductors until it is furnishing quite pure gas.

COST OF PLANT FOR THE SALE OF COMPRESSED GAS.

The cost of a plant of this system for the daily production of 33 metres of oxygen and 66 metres of hydrogen per twenty-four hours is calculated by Schmidt[1] in the following manner.

Site of 1200 square metres	$ 250.00
Building, 150 square metres under roof	2,000.00
Office and dwelling 100 square metres, two stories	3,000.00
1 Boiler, 30 sq. metres h't'g surf., with foundation and chimney	1,250.00
1 Steam engine, with foundation and pipe connections	1,625.00
1 Dynamo, 15.5 kilowatts	412.50
1 Switchboard with instruments	100.00
1 Decomposition cell of 16.5 kilowatts capacity	2,400.00
Accessories, tubing and wire conductors, heating and lighting	1,250.00
1 Gasometer for 20 cubic metres of oxygen, set up	600.00
1 Gasometer for 40 cubic metres of hydrogen, set up	875.00
1 Gas compressor, capacity 50 cubic metres of oxygen per 10 hours	625.00
1 Gas compressor, capacity 100 cubic metres of hydrogen in 10 hours	1,000.00
Miscellaneous, pipe connections, emptying arrangements, etc.	150.00
Belting, shafting	250.00
Furnishings	375.00
Erection, freight, pipe coverings	500.00
1000 steel cylinders, at $10.00	10,000.00
Extras and starting up	1,787.50
Total	$27,500.00

The cost of running and the profits of such a plant are calculated by Schmidt:[1]

COST OF OPERATION FOR THE SALE OF COMPRESSED GAS.

Power. 25 H. P. for the decomposition of water.
5 H. P. for the compression during the day.
30 H. P. total.

Coal 1.5 kg. per H. P.-hour for 300 days of 24 hours each = 330 metric tons, at $3.75 per ton	$ 1,250.00
1 Superintendent	1,000.00

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[1] Private communication to the author.

Brought forward	$2,250.00
1 Workman	625.00
3 Machinists	1,050.00
Lubricants, waste and commutator brushes	500.00
5 per cent. interest on the cost of the plant	1,375.00
10 per cent. sinking fund	2,750.00
Heating, lighting, water	150.00
Extras and repairs	425.00
Total	$ 9,125.00

At the present average selling price of $1 per cubic metre for oxygen and 31¼ cents per cubic metre for hydrogen, allowing a 10 per cent. loss of gas, the income would be:

9000 cubic metres of oxygen, at $1.00	$ 9,000.00
18,000 cubic metres of hydrogen, at 31¼ cents	5,625.00
Total	$14,625.00
Royalties, 10 per cent., about	1,500.00
	$13,125.00
Profit from sale of flasks	375.00
	$13,500.00
Operating expenses	9,125.00
Profit	$ 4,375.00

Allowing about 16 per cent. extra dividends.

In the above, assumptions are made that both gases are sold in the compressed condition; the cost is 33¾ cents per cubic metre. It can plainly be seen that the oxygen determines the condition for a profitable operation of the plant.

The figures work out naturally much more favorably if the gases are used on the spot, where no compression plant is necessary.

When the power needed can be taken from an already existing electrical plant, and in consequence of being part of a work already in operation, no particular clerical force being necessary, the figures are more favorable.

COST OF OPERATION WITHOUT COMPRESSION.

It is therefore worth while to work out separately, for the three possible cases of producing gas, the cost of maintenance, in doing which we will assume the extreme cases in the cost of power, namely ¼ and 1¼ cents per kilowatt hours.

The figures are as follows:

(*a*) FOR DETONATING GAS.

Production of Both Gases, i. e., of Detonating Gas.

The cost of plant is lowered in consequence of the smaller space occupied, the omission of the power and current plant, the compressors, the office and dwelling and the supply of gas containers, to the extent of about $7125.00.

The yearly cost of running would, therefore, be as follows for the respective costs of power per kilowatt hour:

	¼ cent.	1¼ cents.
16.5 kilowatt × 24 hours × 360 days = 142,560 kilowatt hours	$356.25	$1781.25
1 workman	350.00	350.00
Supplies, etc	250.00	250.00
5 per cent. interest on cost of plant	351.25	351.25
10 per cent. sinking fund	712.50	712.50
Heating, lighting, water, repairs, etc	100.00	100.00
Total	$2125.00	$3550.00

The total cost of a cubic metre of detonating gas with a yearly production of 27,000 cubic metres is, therefore, 7¼–13¼ cents per cubic metre.

(*b*) FOR OXYGEN.

Utilization of Oxygen Alone.

As compared with the cost of plant in *a*, there is a reduction in the capital invested to the extent of the hydrogen gasometer with its appendages, so that it will be about $6250.00.

The cost of operation amounts to:

	¼ cent per kilowatt hour.	1¼ cents per kilowatt hour.
Power	$356.25	$1781.25
1 workman	350 00	350.00
Supplies, etc	250.00	250.00
5 per cent. interest	312.50	312.50
10 per cent. sinking fund	625.00	625.00
Not specified	100.00	100.00
Total	$1993.75	$3418.75

The total cost per cubic metre of oxygen, with the yearly production of 9,000 cubic metres is, therefore, 22–38 cents per cubic metre.

(*c*) FOR HYDROGEN.

Utilization of the Hydrogen Alone.

As compared with *a*, the oxygen gasometer is spared, and the cost of the plant will be approximately $6500.00.

The cost of running will be:

	¼ cent per kilowatt hour.	1¼ cents per kilowatt hour.
Power	$365.25	$1781.25
1 workman	350.00	350.00
Supplies, etc	250.00	250.00
5 per cent. interest	325.00	325.00
10 per cent. sinking fund	650.00	650.00
Not specified	100.00	100.00
Total	$2031.25	$3456.25

The total cost per cubic metre of hydrogen, with a yearly production of 18,000 cubic metres, must be 11¼–19¼ cents per cubic metre.

PRACTICE.

The Schmidt arrangement is especially suited for small operations since it is easily adapted to existing direct current lighting plants. In consequence the apparatus has been introduced in a relatively short time in many accumulator works for soldering purposes. At present the following plants are in operation furnished with Schmidt apparatus:

TABLE V.

No.	Plant.	Erected.	Voltage	Amperes.
1	Accumulatorenfabrik Oerlikon	June, 1898	65	15
2	Rheinisches Stahlwerk	March, 1899	110	160
3	Henry Tudor, Rosport, Luxemburg	January, 1900	110	15
4	Soc. Espanola del Acc. Tudor, Zaragoza	March, 1900	70	30
5	Elektroch. Institut des Polyt. Zürich	July, 1900	110	15
6	The Tudor Accum. Co., Ltd. Manchester	August, 1900	70	60
7	Soc. française de l'Acc. Tudor, Lille	September, 1900	110	60
8	Société Tudor, Bruxelles	January, 1901	110	30
9	Fabrik elektrochem. Produkte, Wetzikon	May, 1901	220	30
10	Accumulat.-Fabr. Oerlikon, Enlargement	June, 1901	65	30
11	Soc. ital. del Carburo di Calcio, Terni	September, 1901	110	30

The manufacture and the introduction of the Schmidt Water-electrolyzer has been undertaken by the Machinenfabrick Oerlikon of Zurich, Switzerland.

(b) With Complete Non-Conducting Partitions.

(a) *For Instruction and Laboratory Apparatus.*

A demonstration apparatus for the electrolysis of water using complete non-conducting partitions, and which separates the gas evolved, is used particularly for lecture purposes, in order to show clearly that water consists of two volumes of hydrogen combined with one volume of oxygen.

RITTER'S APPARATUS.

As Ostwald[1] incisively remarked, we find the "prototype of the present widely used forms of apparatus," in the arrangement shown more than a century ago by Ritter[2], two of whose best apparatus are reproduced in Figs. 21 and 22, for the purpose of comparison.

In this group of apparatus, intended especially for purposes of instruction, the conductivity of the water to be decomposed is increased by additions. Usually an 8–10 per cent. solution of sulphuric acid is employed.

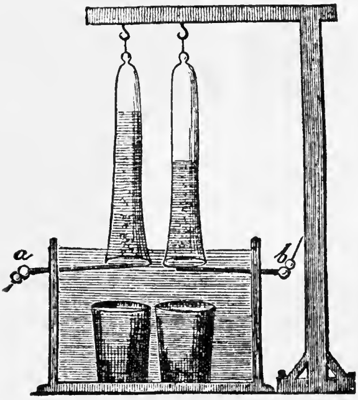

Fig. 21.

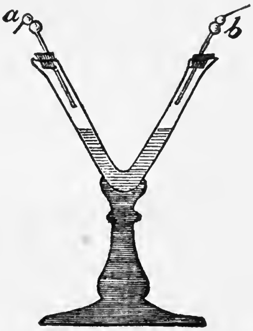

Fig. 22.

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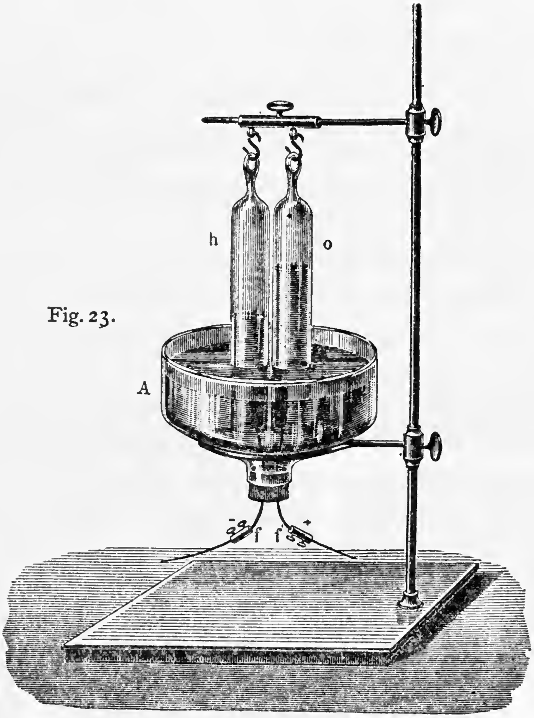
[1] Ostwald: Elektrochemie, ihre Geschichte und Lehre, 1890, p. 162.

[2] Voigt's Magazin für den neuesten Zustand der Naturkunde, **2**, 356, 1800.

FORMS OF THE APPARATUS.

One of the simplest apparatus which is yet in use is shown in Fig. 23[1]. Two platinum wires pass through the neck of the vessel *a*, ending in platinum poles, one connected with the + pole and the other with the — pole of a galvanic battery. The quantities of gas evolved can be read off on a graduated glass tube not far above the electrodes. The tubes are naturally filled with electrolyte before the current is turned on. Since oxygen is more soluble in the electrolyte than hydrogen, and since a small quantity of ozone always forms at the + pole, there is obtained under the usual conditions somewhat less than one volume of oxygen to two volumes of hydrogen. The formation of ozone is diminished by heating the

Fig. 23.



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[1] Graham-Otto: Lehrbuch der Chemie, II, 1, 146.

water, and a more correct relation between the gas volumes is thus obtained.

HOFMANN'S APPARATUS.

The forms of apparatus most in use are based upon the construction described by A. W. Hofmann. One of the newest forms is that pictured in Fig. 24.

The apparatus consists of a U-tube for the reception of the electrolyte (acid or alkaline water). The arms of the same are somewhat long and are closed above with stop-cocks. Platinum wires are melted into the lower part of the arms and carry the sheet platinum electrodes. The fluid forced out by the evolution of gas passes through a rubber tube into an adjustable reservoir. If the current is allowed to pass some time the gas volumes can be easily read off, and by letting them escape through the stop-cocks each can be recognized by its characteristic reactions. Likewise the presence of ozone may be determined when using acidulated water at low temperatures.

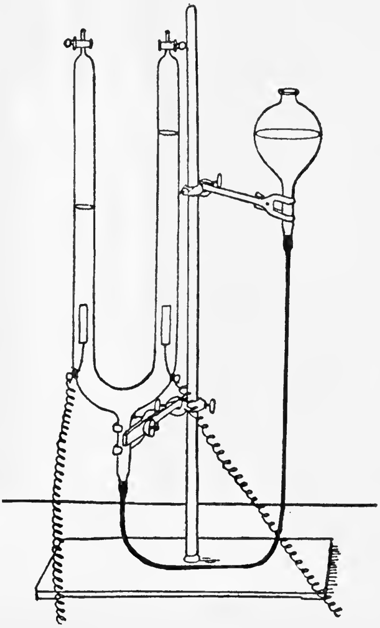

Fig. 24.

The apparatus has the advantage that the influence of the absorption of the electrolyte may be avoided by running the apparatus some time before closing the stop-cocks, and the gas can be brought up to any desired pressure by raising the reservoir.

The improvements of the Hofmann Electrolyzer consisting in a device for preventing overflow, and the use of exchangeable glass caps on the platinum electrodes has been patented by Geissler & Co., of Berlin, in the German patent 157,840 of the 6th of June, 1901.

If it is desired to produce a gas especially rich in ozone for purposes of demonstration, the concentration of the sulphuric acid used is increased, taking one volume of concentrated sulphuric acid to five or six volumes of water. The current density is also increased by using in place of foil fine wires of platinum or platinum iridium as electrodes. Finally the temperature of the electrolyte is kept as low as possible. In this manner, for instance, Soret[1] obtained at a temperature of 5–6° C. 3 per cent. of ozone, and by cooling with ice and salt as high as 6 per cent.

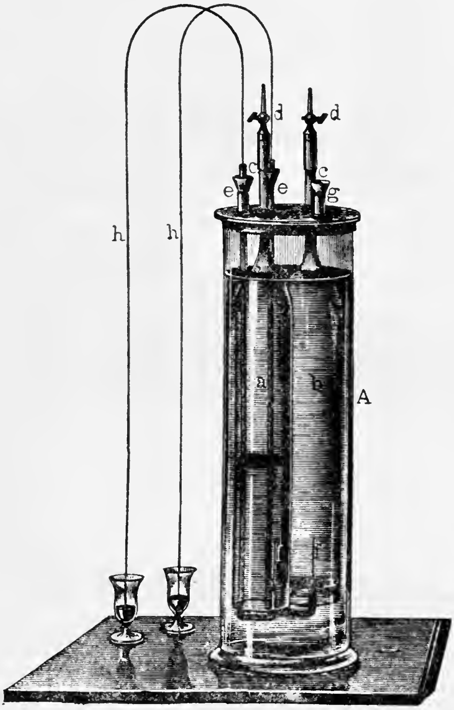

Fig. 25.

BUFF'S APPARATUS.

An apparatus especially designed for the manufacture of oxygen rich in ozone, is described by Buff.[2] It is shown in Fig. 25, which is intelligible without further description.

ROSENFELD'S APPARATUS.

A demonstration apparatus, which can be constructed with the simplest materials and with all the parts easily

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[1] Poggendorf's Annalen.

[2] Graham-Otto, "Lehrbuch der Chemie," II, 1, 84.

replaceable, devised by M. Rosenfeld, is shown in Fig. 26.[1] This consists of a cylinder, *c*, 7 cm. high and 3 cm. wide, provided with two well fitting, rubber stoppers, the upper one of which carries two gas-collecting tubes 70 cm. high and 1 cm. in diameter, provided with stop-cocks. The lower stopper having 3 holes, carries the 2 electrodes and the glass tube *r*, to which is attached by means of the rubber tube *s*, a funnel, *t*. The gas-collecting tubes, which at equal heights must possess exactly equal volumes, reach down almost to the lower stopper, while the smaller tube *r* projects 5 mm. inside the cylinder. The electrodes are about 6 cm. higher than the cylinder. The apparatus allows volumetric investigations to be made in the shortest time with feeble currents. Warming of the electrolyte is to be recommended and can be accomplished by passing a gas flame around the tube.

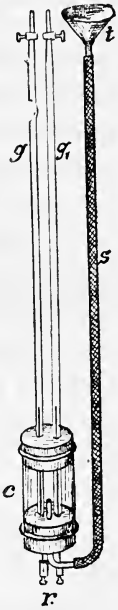

Fig. 26.

REBENSTORFF'S APPARATUS.

Rebenstorff[2] has proposed to use the Hofmann principle for decomposing water, as a voltameter. In this case the filling funnel must be connected with the apparatus, not by a rubber tube, but by a glass tube firmly fastened to the U-tube, as was the case with the older Hofmann arrangement. Two marks are then placed upon the funnel tube, and the time is measured in which it takes the fluid to rise in this funnel tube from the lower to the upper mark, in consequence of the evolution of gas in the U-tube. The placing of the lower mark is a matter of no importance. The upper mark should be so placed that when using the apparatus as a voltameter no reduction of the volume of the gas to normal pressure is necessary on account

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[1] Zeitschr. phys. und chem. Unterr., 1900, **13**, 261. Chem. Ztg. Repertorium, 1900, **43**, 373.

[2] Zeitschr. phys. und chem. Unterr., 1900, **13**, 332. Chem. Ztg. Repertorium, 1900, **43**, 373.

of the greater density of the sulphuric acid. This is the case if the upper mark is approximately at the height of the first one-third of the difference of level of the two columns of liquid after the electrolysis is stopped. If the marks are placed in the proper manner, it only remains to determine the volume of gas produced during the rise of the fluid from the lower to the higher mark. Several measurements are taken and the average volume found, reduced to 0° C. and the normal barometer pressure, correcting for the tension of water vapor.

HABERMANN'S APPARATUS.

Habermann[1] proposes to make the bell of the latter apparatus, shown in Fig. 27, of semi-circular section in order to diminish as far as possible the distance of the electrodes apart. He obtains with this arrangement a very considerable decomposition of water with a thermal element of fifty couples, especially if the electrodes reach down nearly to the lower edge of the gas bell. The gas bells *B* are contained in a vessel, *A*, and are fixed thereto by means of the stopper *C*. The bells terminate above in round tubes which are provided with two tube connections *D D*. The bells are held fast at *F* by a flat piece of cork and binding twine.

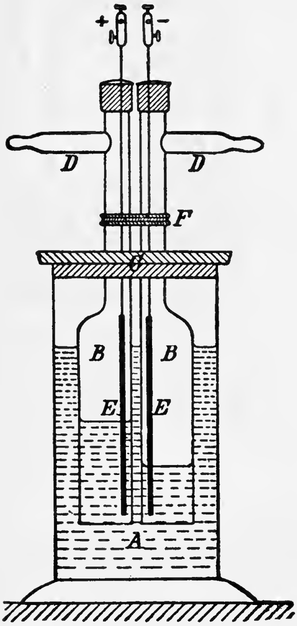

Fig. 27

If palladium cathodes are used in the electrolysis of acidulated water, we observe, according to Graham[2], quite considerable quantities of hydrogen and fully four times as much when using wire cathodes as sheet cathodes. Glad-

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[1] Zeitschr. für ang. Chemie, 1892, 323–328.

[2] Compt. rend., 1869, 68, 101. Pogg. Ann., 1869, 136, 317 und 1069.

stone and Tribe have investigated the strong reducing qualities of the occluded hydrogen.

(*b*) *For Technical Purposes.*

The fundamental idea underlying the demonstration apparatus, that is, the use of bells of non-conducting material covering over the electrodes, has also been taken advantage of by several investigators in technical apparatus, but without much successful application in practice.

Process of Ascherl, 1894.

E. Ascherl obtained an Austrian patent 44/5862, Nov. 9, 1894, dating from September 26, 1894, for an "Apparatus for decomposing water by means of dynamo currents and for the drawing off of the evolved gases."

PATENT CLAIM.

The patent claim reads:

1. "An apparatus for the decomposition of water by means of dynamo currents, characterized by an insulated decomposition vessel, *a*, with two gas bells, *b b'*, beneath which are metallic wire brushes, *d*, connecting with the necessary conducting wires of the dynamo machine and which may be set in reciprocating motion by a shaft, whereby the gas collecting on the brushes and shaken therefrom, is collected by the bells and led away by the collecting tubes *g* and *h*."

2. "In combination with the apparatus described under 1, an arrangement for drawing off of the gas from the collecting reservoir, consisting of the receivers *k k'*, placed in water holders, *l l'*, and communicating on one side with the collecting tubes *g h*, and on the other side in connection with the gas pumps, so that by the sinking of water previously pumped into the receivers, suction is produced in the vessel *a*."

DESCRIPTION.

In the adjacent drawings, Fig. 28 shows the apparatus in section, Fig. 29 in plan, and Fig. 30 shows a front view of the decomposing apparatus.

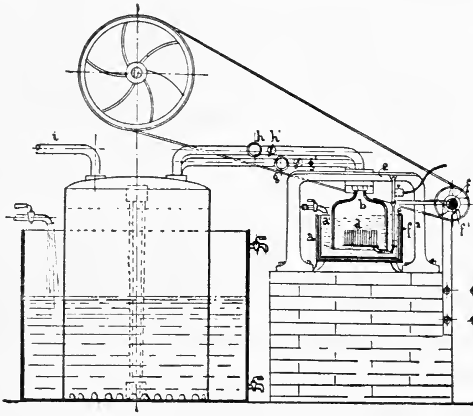

Fig. 28.

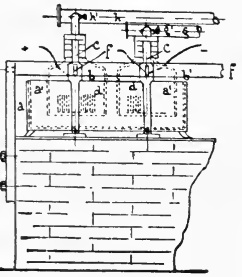

Fig. 30.

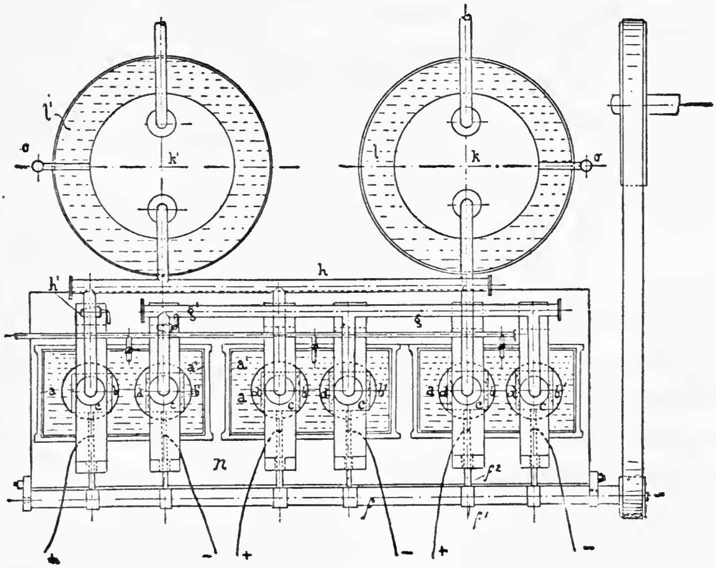

Fig. 29.

The decomposing apparatus consists, as is easily seen from the drawings, of a number of decomposing vessels, *a*, filled with acidulated water, made of wood or metal, which are lined inside for better insulation with glass plates, *a'*. Two glass bells, *b* and *b'*, dip into each of these vessels and are fastened to the separators *c* and covered with brushes of silver or platinum wires *d*, upon which the gas, formed by decomposition, is set free. To liberate the gas generated from the brushes and thus get constant action of the current and quicker decomposition of the water, the brushes are fastened to levers *e* made of hard rubber and which are capable of being rotated on the supports *c*, and given a quick reciprocating motion by means of the eccentric f^1 on a shaft *f* driven in any suitable manner by means of the eccentric rods f^2.

The strong copper wires are placed in the lever *e* and connected with the metallic wire brushes and serve for conducting the current. The + pole of the dynamo machine being with one of the brushes under the glass bell *b* and the — pole with the brush under the bell *b'*.

The decomposition vessels *a* are placed upon an insulating foundation *n* (of asphalt) to prevent loss of current.

As soon as the current is put on, decomposition of water takes place; to keep the hydrogen and oxygen accumulating in the gas chambers separated from each other, all the glass bells *b* are connected with the gas collecting tube *h*, and all the glass bells *b'* with the collecting tube *g*.

These tubes are provided with the regulating valves *g' h'*, and lead to the reservoirs *k* or *k'* which are securely placed in the open water containers *l l'*, with which they are in communication by the openings *m* near the bottom.

The receptacles serve for sucking off the gas and are provided with the water-gauges *o*, and are in communication with the gas pumps by the tube *i*, while the containers *l l'* are furnished with inlet and outlet cocks. When the gas formed in the apparatus and collected in the bells *b b'* is to be withdrawn, the cocks *g' h'* are first closed and the receivers *k k'* put in communication with the gas pumps, which latter convey the gas to the gasometers. When pumping out the reservoirs, the water rises in the same nearly to the top, whereupon the cocks *g' h'* are opened. The latter thus sink into

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the receivers; water flows into them and exerts a suction upon the gases which are coming out of the tubes *g h*. By completely letting out the water by means of the run-off cocks of the holders *l l'*, the reservoirs *k k'* can be completely filled with gas, which is then sucked off by the pumps to the gasometers.

In the author's opinion, the whole arrangement contains no new principle with the exception of the motion of the electrodes for purpose of diminishing the polarization. If the latter purpose is to be achieved by mechanical power, however, many other means of doing it may be found which will obtain it in a simpler manner. The proposed use of silver as electrode material is not permissible with acid electrolytes.

PRACTICE.

The apparatus has not been industrially applied. With the exception of a demonstration apparatus in a glass works in Bohemia,[1] no further installation has been made. The apparatus was invented for supplying the oxyhydrogen flame.

The process of the Electricität Aktien-Gesellschaft, formerly Schuckert & Co., of Nuremberg, is discussed in the division A (c), although it works with partitions of non-conducting material, since in other respects it comes nearest to the Garuti apparatus.

Process of Schoop, 1900.

The recently developed construction of M. U. Schoop may also be placed in this group of apparatus. The German registered design for the same, 141,049, of September 5, 1900, contains the following claim:

PATENT CLAIM.

"Electrolytic apparatus for the decomposition of water characterized by solid or hollow electrodes of sheet lead or steel arranged at the same distance from the base, each set in

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[1] Zeitschrift. f. Elektrot., Wien., 1895, 551.

a glass or clay tube perforated beneath and hermetically closed above."

It is easily seen from Schoop's final patent claim, Austrian patent 1285 of 1900, what he regards as new in his arrangement:

1. "Electrolytic apparatus for the decomposition of water consisting of an electrolyte holder acting as anode whose floor is protected from contact with the electrolyte by an insulating covering, and a number of tube-shaped cathodes resting upon these insulating layers, each of which is surrounded by a closed glass or clay tube reaching nearly to their lower ends, and closed above, the said cathodes being perforated at their lower free ends where they are not surrounded by the enclosing tubes, through which perforations the electrolyte circulates freely, and through which the gas set free between the insulating tubes and the cathode tubes passes into the interior of the latter, and thence through conducting tubes to the gasometer or other places where used."

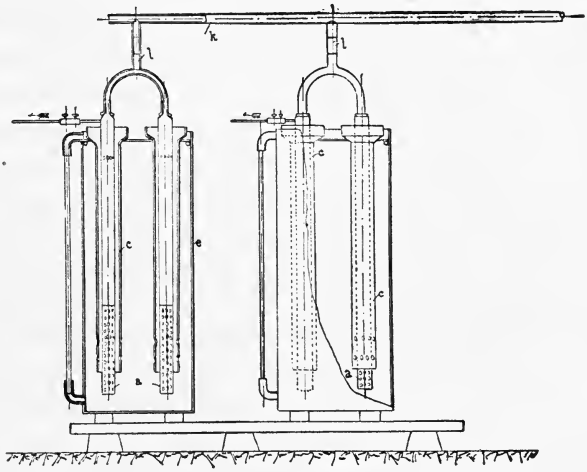
2. "An altered form of the decomposition apparatus described in 1 in which instead of the electrolyte holders acting as cathodes, cathodes analogous to the anodes are employed consisting of lead tubes surrounded by glass or clay tubes which permit the collection of the hydrogen in the same manner as designated for the oxygen under claim 1."

FORM OF APPARATUS.

Fig. 31 shows a schematic drawing of the Schoop apparatus. It consists of two decomposition cells united with each other, each containing four electrodes, *viz.*, two anodes and two cathodes.

The tubular electrodes *a* are hung in enlargements of the glass or clay tubes *c*. The hermetical sealing of the electrodes in the surrounding tubes is obtained by pouring melted material around the upper end. The lower part of the tube *c* is perforated.

The electrode tubes *a* are perforated half way up and filled inside with fine lead wires in order that the evolution of gas may take place outside as well as inside of the tube with equal intensity. Besides this there is at the upper end of the tubular electrode *a*, a passage for the escape of the gas. The electrodes are connected in pairs to their common collecting tube *k*. This connection with the collecting tube is effected by using a short connecting tube of non-conducting material in order that the single cells may be insulated from each other.



Each reservoir, *e*, is provided with a water-gauge for observing the level of the acid.

From the preceding, it may be seen that Schoop did not carry out his idea described in his patent claim of the Austrian patent, namely, that of using a vessel as anode and tubular electrodes as cathodes, while the bottom of the vessel was insulated. This arrangement has also numerous shortcomings.

Leaving out of consideration that the utilization of the electrodes, which is not very good in the apparatus in general, is not improved by this arrangement, the use of insulating material in the electrolytic apparatus possesses many difficulties. It is, moreover, difficult to find an insulating material (resin or solid hydrocarbons) which possesses a constant consistency at all temperatures to which it may be subjected. If cracks once appear in this insulation at the bottom, the hydrogen becomes at once contaminated with oxygen. On the other hand, with the arrangement chosen the greatest current density would be expected at the border between the anode vessel and the insulating material. Oxidation of the organic insulating material would follow, as has been observed with the Schmidt apparatus with the rubber edges of the asbestos diaphragms, and thus unavoidable contamination of the oxygen would result.

Fig. 32[1] shows a view of the first experimental plant with

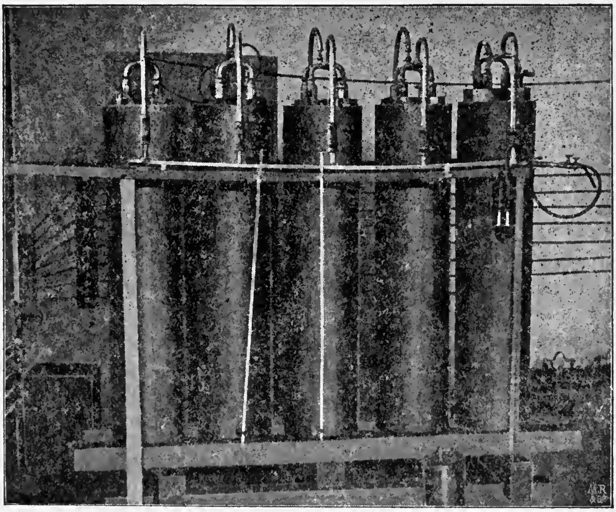


Fig. 32.

which Schoop tested his system on a large scale. Schoop claims for his apparatus[2] a greater security in operation than in any of the systems working with diaphragms, a perfect purity of the gases, and ascribes to the diaphragm apparatus further, the disadvantage that with even small variations of density in the diaphragms, diffusion can occur to such an ex-

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[1] From an original photograph.

[2] Zeitschrift f. Elektrot., Wien, 1900, **37**, 444. Eclairage électr. (1900), **21**, 50. Elektro-chem. Zeitschrift, 1900–'01, **10**, 224.

tent that the hydrogen may contain up to the danger limit of 6 per cent. of oxygen, which may lead to explosions. The resistance of the apparatus is higher than in other systems.[1]

The gases escape under about one metre of water column. They are entirely freed from acid carried over by passing them through milk of lime before entering the gasometer; the apparatus needs to be taken apart only after several months operation. The electrodes are said not to be attacked; hard lead is recommended as the best material for them.

OUTPUT.

Schoop gives as the output of his apparatus 68 litres of oxygen, and 136 litres of hydrogen per electrical H. P. Assuming a nearly theoretical current output, these figures would correspond to a working tension of 2¼ volts. Since Schoop says at one place when using lead electrodes with acid electrolyte an electromotive force of 2.5 to 3.5 volts per apparatus may suffice for creating the current density, it may be assumed that the output before mentioned applied to iron electrodes with alkaline electrolyte, which manner of working is also described by Schoop as possible, but as entailing a high cost of plant.

COST OF OPERATION.

Upon these figures we may calculate that every 3 cubic metres of mixed gas requires 10.82 kilowatt hours, costing at ¼–1¼ cents per kilowatt hour the following:

1 cubic metre of detonating gas	0.9 – 4.5	cents.
1 cubic metre of hydrogen	1.35– 6.75	"
1 cubic metre of oxygen	2.70–13.50	"

when using iron electrodes.

Using acid electrolyte (sulphuric acid of a specific gravity of 1.235) and lead electrodes, Schoop[1] says, from the data obtained in operating a plant in question, that a voltage of 3.9 is needed with cold acid and 3.6 with warm acid. From this

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[1] Private communication to the author.

data, assuming a theoretical current output and 3.5 volts to be used, there is required 18.67 kilowatt hours for producing 3 cubic metres of mixed gas, and the cost of production with power at ¼ and 1¼ cents per kilowatt hour is respectively:

1 cubic metre of detonating gas	1.550– 7.750 cents.
1 cubic metre of hydrogen	2.325–14.625 "
1 cubic metre of oxygen	4.650–23.250 "

PRACTICE.

The Schoop water decomposition apparatus was tried in an experimental plant of small capacity by the Cologne Accumulator Works of G. Hagen, at Kalk on the Rhine, and this firm erected a plant for a total daily production of 15 to 20 cubic metres of hydrogen and 7.5 to 10 cubic metres of oxygen.

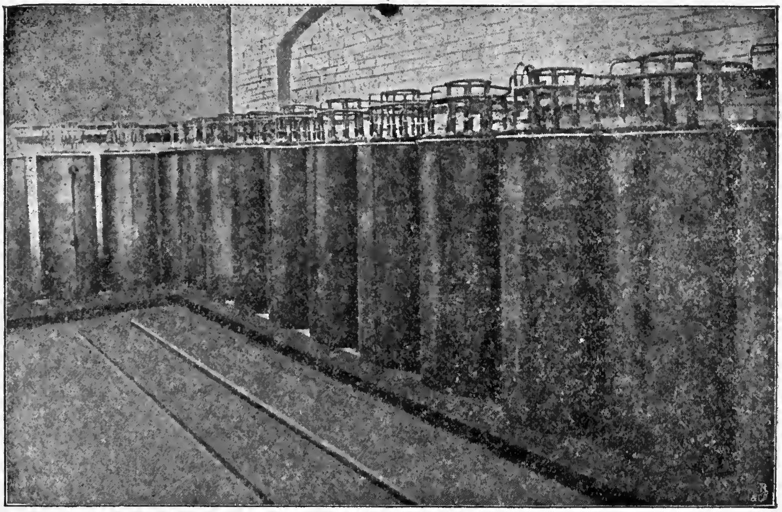

Fig. 33.

The plant consisted of 18 cells connected in series, through which was sent 150 to 200 amperes. The switchboard contained: 1 Weston ammeter for 250 amperes, 1 voltameter, 1 indicator of the direction of the current, 1 low current cut out, 1 signal bell, and 2 water manometers. The current was furnished by a shunt-wound dynamo of 250 amperes and 65 volts. The primary cost of the plant was approximately $1,250, and the operation of the same resulted in a saving of $1,750 yearly, as compared with the previous method of manufacture of hydrogen for soldering purposes. Fig. 33 shows part of this plant.

The same firm has undertaken the construction of the Schoop apparatus for foreign customers.

Process of Hazard-Flamand, 1898.

If we do not confine ourselves exclusively to the electrolysis of water, the Hazard-Flamand apparatus may be classified with this group of apparatus. It was patented in Germany, No. 106,499, of June 12, 1898.[1]

FORM OF APPARATUS.

The inventor describes his construction as a "water-sealed diaphragm" for electrolytic apparatus, especially for the electrolysis of water. The principal idea of the diaphragm, which is intended for the general manufacture of gas, and which prevents mixing of the anode and cathode fluids saturated with their respective gases, is shown in Figs. 34 and 35.

In the box *A*, which forms the cathode and is provided with ribs, *a*, for increasing the lateral surface are transverse partitions, a', cast in one piece with the box *A*, and likewise ribbed a_2 for increasing the surface. The deep gutter *B* is filled with an insulating fluid and receives the edge of the cover *M*. The cover is insulated from the vessel containing the electrolyte by the ebonite blocks B′. The clamping screw *D* conducts the current. In the chamber formed by the transverse partitions a' is the anode *E*, likewise provided with ribs *e*; e^1 is the conductor which is led through the cover and insulated therefrom. The anode is arranged in a bell, e^2, and projects into the cylindrical holder m^2. The latter is in one piece with the cover and closed in, gas-tight, with paraffin. The several positive electrodes are naturally connected in parallel. The an-

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[1] Zeitschrift f. Elektroch., 1899–1900, 511.

odes are surrounded by diaphragms, which consist of long gutters, H, of Y-shaped section made of ebonite, porcelain, glass, etc. The upper parts of these run underneath, almost touching the bottom of the next gutter below. The rings

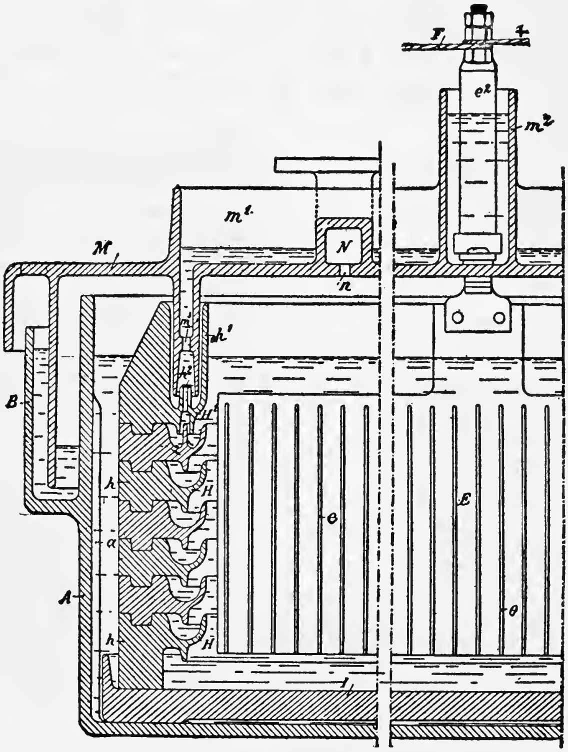

Fig. 34.

have attachments, *h* (Fig. 34), in order to hold them tightly in place. The lower ring rests with its side projections upon the insulated cap *I*, which latter has the function of preventing hydrogen evolved from the bottom of the vessel from passing into the anode chambers. The uppermost ring *H* is of a different shape from the others for the purpose of closing perfectly the anode cells. The cover *M* projects downwards into the uppermost gutter *h'* by means of the circular flange *m*.

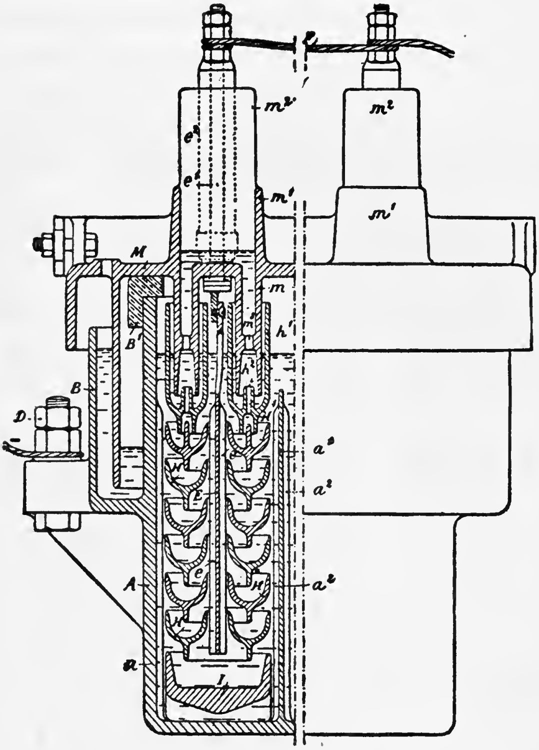

Fig 35

The gases are collected in two canals, *N*, in the cover, connected by suitable openings, *n*, in the respective cells. The pipe connections branch from these canals. The flanges m^1 in the cover are the containers which communicate with the inside of the decomposition vessel and are filled with electrolyte. This prevents escape of gas from the openings h^2 and m^3. While the apparatus is in action, if the level of the fluid in m^1 varies through inattention, the gas will escape into the air through m^3, but without mixing in the apparatus. Likewise, no mixing of gas takes place if the internal pressure rises because of irregularities in the conducting off of the gas, as in that case the gas escapes from the apparatus as soon as the level of the liquid has sunk to the lower edge of the bell *m*.

PRACTICE.

Nothing is known of any industrial application of this somewhat complicated apparatus.

Process of Verney, 1899.

A similar idea is embodied in P. J. F. Verney's invention, French patent 280,374[1].

This apparatus is intended primarily for the electrolytic decomposition of water, but is also suitable for the decomposition of other electrolytes, for the purpose of obtaining gas.

FORM OF APPARATUS.

The apparatus consists of a metallic box, divided above into a number of chambers by a series of partitions cast in one piece with the external shell. The external vessel with its partitions serves for one pole and the other pole is formed of metallic sheets contained in the compartments of the box. Insulating rings of Y-shaped section are arranged around these grooved sheet electrodes, the downward-plunging part of each ring extending into the cover-shaped enlargement of the ring beneath, without, however, touching it. By this means sufficient permeability section for the current is provided, with at the same time complete separation of the gases.

This is therefore a patenting of the same subject under two different names.

PRACTICE.

Verney's apparatus had no application in practice at least as far as the author can learn.

Both of the latter described apparatus remind one in many ways of the curtain diaphragms such as have been proposed for the technical electrolysis of the alkaline chlorides.

(c) With Complete or Perforated Conducting Partitions.

Process of Garuti, 1893.

P. Garuti introduced a new principle as far as concerns the

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[1] L'Ind. électro-chim., III (1899), 31.

practical operation of electrolytic apparatus for decomposing water. In the first claim of his German patent of July 25, 1892, he specifies the following improvements:

PATENT CLAIM.

"An electrolytic apparatus characterized by the use of partial metallic partitions between the cells containing the two electrodes, whereby the tension used is so reduced that no permanent decomposition takes place at the partition but the principal current passes through the opening in the partition, for the purpose of obtaining cells of greater strength and resistance against the influence of the electrolyte than is obtained by the use of the old materials, and yet to completely prevent the danger of a reunion of the final products (formation of detonating gas).

Several good descriptions of the principle of this new idea of Garuti's have appeared in the Italian technical journals.[1] Garuti claimed that the diaphragms used previously to his invention have too high resistance, are used up too quickly, and therefore require too many renewals. He claims that even the best diaphragms still possess the possibility of allowing a partial admixture of gas to take place, as well as the formation of precipitates in the pores of the diaphragm which increase the resistance of the same.

PRINCIPLE.

It is a fact that before Garuti no one had thought of using complete metallic plates in the electrolysis of water, since the latter should, according to the theory of intermediate electrodes (bipolar), evolve on the side towards the anode some hydrogen, and on the side towards the cathode some oxygen, a principle which is made use of practically in many forms of apparatus.

If we bring into a vessel filled with acidulated water (Fig. 36), two electrodes, and separate the same by a metallic par-

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[1] L'Elettricità, 1899, **37**, 502; L'Ind. électo-chim., **III**, 113.

tition *c*, (Fig. 37), there is formed two separate decomposing cells and the partition acts as a bipolar electrode evolving hydrogen in the anode compartment and oxygen in the cathode compartment.

Since, as has frequently been mentioned, the electrolytic decomposition of water requires approximately 1.5 volts, with the introduction of the plate we require at least 3 volts tension to produce it since evolution of gas takes place at both surfaces of the secondary electrode. If the partition is, however, raised so that the fluids in *M* and *N* can communicate by a passage as is shown in Fig. 38, and the voltage used between *a* and *b* is correspondingly reduced, this evolution of gas occurs only at the end electrodes and not upon the metallic partition. The partition will, therefore, act only as a bipolar electrode, when we employ more than 3 volts tension between the poles *a* and *b*. The metallic partition, therefore, takes no part in the electrolysis as long as the tension used is not very much greater than that needed for a single decomposition cell.

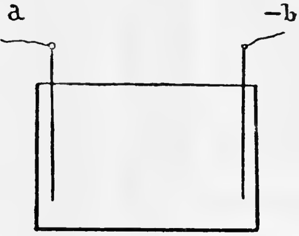

Fig. 36.

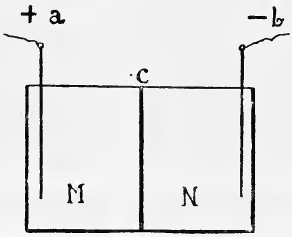

Fig. 37.

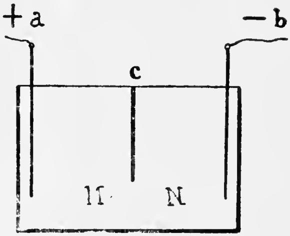

Fig. 38.

According to a recent communication of Buffa[1], the priority of this observation is due to the Italian Del Proposto, while Garuti, in company with Pompili, applied the idea technically for the construction of various forms of apparatus for the electrolytic decomposition of water.

According to the patent application of Garuti, previously alluded to, the fundamental form of the apparatus may be described in the following words:

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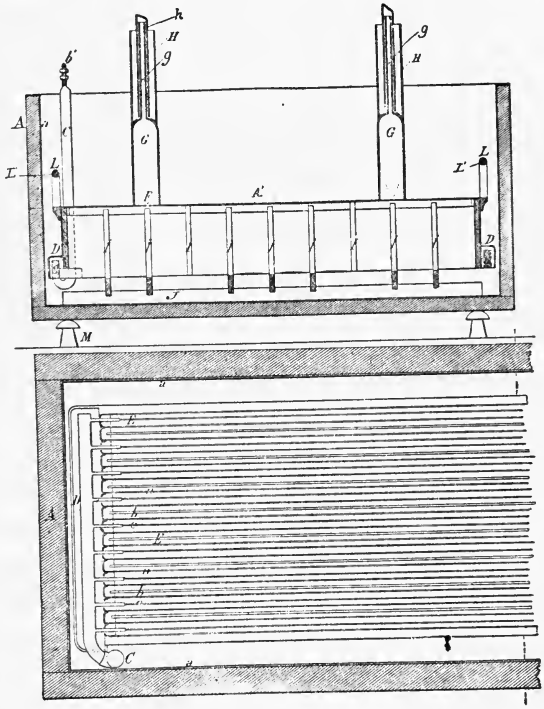
[1] Bulletin de l'Associat. des Ing. Electr., 11, 305 (1900).

FORM OF APPARATUS.

"A practical form of apparatus characterized by a holder or container in the form of a gasometer bell dipping into the electrolyte and provided with two collecting chambers surrounding the electrodes, and to the walls of which are soldered metallic diaphragms parallel to each other and hermetically tight, for the purpose of accelerating the separation of the evolved gases from the electrodes, to give to the gas the necessary pressure for their use and to make irregularities in their production at once perceptible."

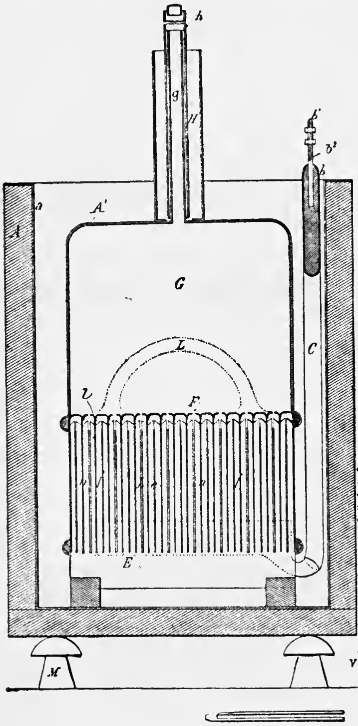


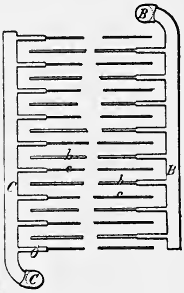
Figs. 39 and 40.

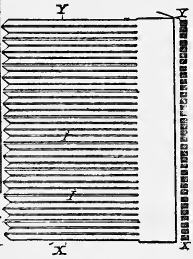
Garuti used, in his first apparatus, electrodes, supports and even vessels of lead.

The drawings of the first Garuti apparatus referred, as far as can be learned from the patent description, to a model left with the German office, suitable for a current of 17 amperes.

The apparatus as shown in Figs. 39–44 consists of a wooden box *A* lined with sheet lead *a*. This box holds the electrolyte as well as the electrolyzing apparatus itself, and stands upon insulators *M*. Twelve per cent. sulphuric acid is used as electrolyte with lead electrodes.







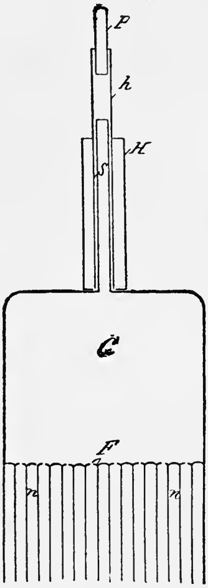


Fig. 41.

Fig. 42

Fig. 43.

The real electrolyzing apparatus consists of a rectangular box open beneath, Fig. 43, divided by metallic plates into long, narrow divisions *n*. These plates form the metallic walls for the separation of the gases. The electrodes are introduced into the chamber thus formed by means of the wooden comb Fig. 44, which serves at the same time for insulating the electrodes from each other and the metallic partitions. Fig. 40 shows best in its horizontal section the arrangement of the electrodes, their connection with the main electrical conductors, as well as the position of the partition walls, *n* being the metallic diaphragms, *cC* the one pole, *b* the end of the other pole.

The distance of the electrodes apart is 10–20 mm., the height of the electrodes 140 mm.; the anodes are somewhat heavier than the cathodes to allow for the production of superoxide, the former being about 3 mm. in thickness, and the latter 1 mm.

The electrodes are prevented from coming in contact with the bottom of the inverted diaphragm chest by means of fork-shaped pieces of wood resting upon (Fig. 44) similar perforated pieces of wood. Naturally the electrodes stand free from the end surfaces of the box. Likewise also, the connecting pieces *O* (Fig. 42), which connect in parallel the electrodes of like polarity, must be insulated from the back walls of the diaphragm chest. When the insulating parts are removed, both systems of electrodes may be easily lifted sideways out of the diaphragm chest. The conductors are fastened to the screw-clamps b^1 b^2 (Fig. 41). The spaces formed by the diaphragms are alternately perforated and their exits are united with two parallel-arranged gas collectors *G* (Figs. 41 and 43). The height of these chambers, which serve likewise to regulate the pressure, must be changed with the pressure desired. The gases pass from these chambers by the lead tube *S*. Above these exit tubes are wider tubes *h*, made of insulating material (porcelain or glass), and the main gas conductors connect only to these in order to insulate the apparatus electrically. A

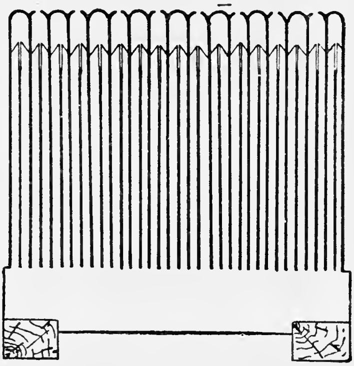


Fig. 44.

lead tube *H*, likewise soldered to the gas chamber allows a gas-tight joint to be made by filling with water between *H* and *S*.

The whole system of electrodes and partitions rests upon two wooden stringers 6 cm. high in order to avoid any short circuits in consequence of the falling down of peroxide and stopping up of the apparatus by precipitation from the electrolyte. Two iron handles, *L* (Fig. 41), covered with lead, permit the whole system to be raised out of the box. Two amperes per sq. dm. is described as a suitable current density for dilute sulphuric acid of the above given concentration.

VARIATION OF APPARATUS.

Garuti describes in his German patent still another modified form of his apparatus which makes a separation of the gases good enough for industrial purposes. This is shown in Figs. 45 and 46.

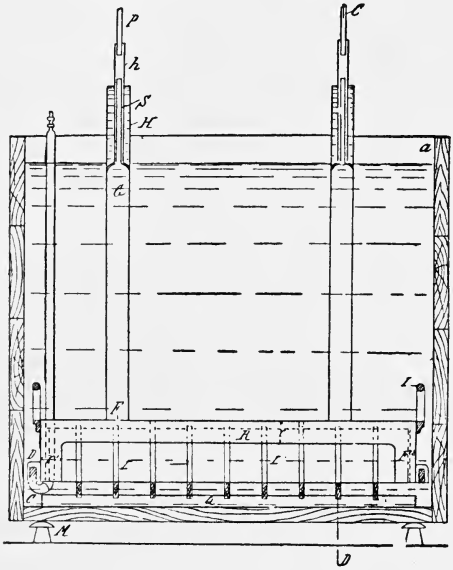


Fig. 45.

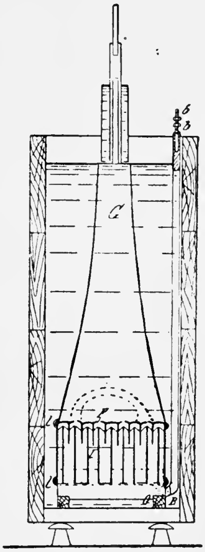


Fig. 46.

The most important difference between this modification and the previously described apparatus consists in an enlargement of the distance between the electrodes to about 30 mm. and an alteration in the form of the partitions. The latter are not at the same height in the whole apparatus, but diminish towards the middle of the apparatus so that the effective electrode surface is increased. This results naturally in a greater danger of the formation of mixed gas, which, however, is taken care of by the greater distance between the electrodes and the higher water pressure. The chamber *G* must therefore be correspondingly deeper. By this arrangement Garuti intends to use a current density of 4 amperes per sq. dm. with a voltage not higher than in the type of apparatus previously described.

The testing of the Garuti cell in practice, and the experience accumulated therewith, made the introduction of various improvements necessary. According to communications in the technical journals of 1899[1], Garuti has dropped the use of lead for the electrodes and partitions. These changes are rendered necessary by the irregular action of the formation of superoxides and particularly also by the weakness of the lead which, by getting out of shape, made very disagreeable short circuits possible in such an apparatus, with very narrow chambers. Garuti therefore passes, as other inventors before him, to the use of iron. This requires also a change in the electrolyte, which Garuti likewise changed to caustic alkali solution.

The improved apparatus (Fig. 47–50), retains its general form, but the outer box as well as the electrode system is of iron.

The distance of the electrodes from each other is decreased to 12 mm. in order to increase the efficiency of the apparatus while the distance of the lower edge of the electrodes from the bottom of the containing vessel is reduced to 12 cm. The partitions are no longer entire but have a zone of fine perforations 4 cm. wide placed by Garuti at first at the lower edge

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[1] L'Elettricità, 1899, **37**, 502; L'Ind. électro-chim. **11**, 113 (1899).

of the electrodes, according to Fig. 48, and later at the level of the middle of the electrodes, as shown in Fig. 49. These two alterations form the substance of the German patents 83,079 and 106,226, which, however, are not taken out in the name of Garuti, but by the German license—the Société anonyme l'Oxyhydrique, of Brussels. The corresponding English patents are those of Garuti and Pompili, numbers 23,663/96 and 12,950/1900.

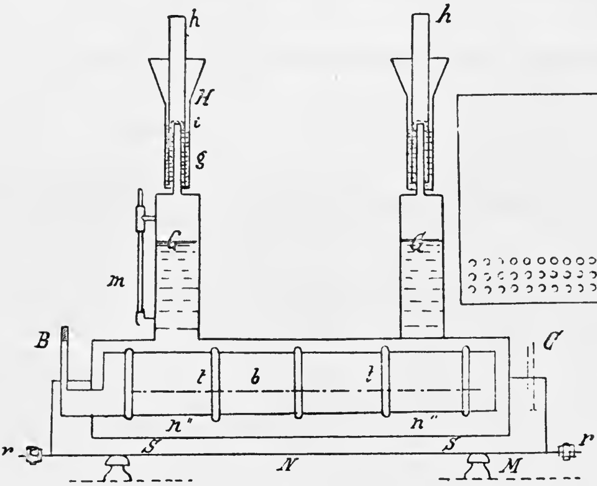

Fig. 47.

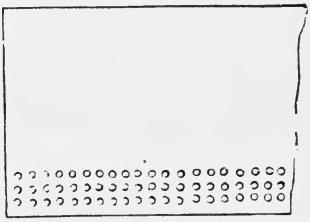

Fig. 48.

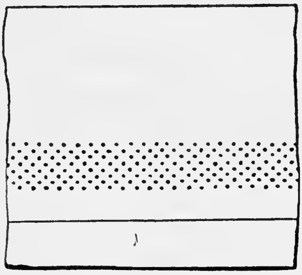

Fig. 49.

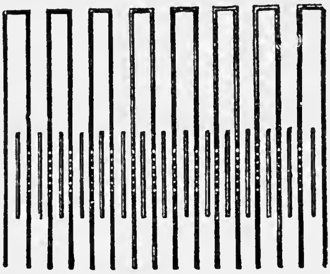

Fig. 50.

In the latter patents Garuti also describes a new form of diaphragm chamber, the length of which in the older type of apparatus is often two metres, causing considerable difficulty in its manufacture.

The new manner of manufacture and connecting up the diaphragm chamber consists in the following:

A rectangular sheet of the length of the electrolyzer and about twice as high is cut through along the middle line *b c* (Fig. 51) somewhat over half way, and thereby divided into three parts *e f g*. The two laps *e f* are now bent over along the lines *j i h* at right angles, but in opposite directions. The sheet represents thereby the shape shown in plan in Fig. 52, in section in Fig. 54, in perspective in Fig. 53.

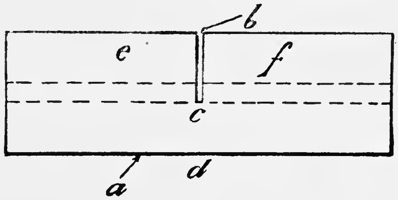

Fig. 51.

Fig. 52.

This forms two cell-like spaces, *m* and *n*, each having a length of half the sheet used. In building up the diaphragm chest from such pieces, each edge *k* of one piece is connected with the edge *l* of the next box. The combination of two such elements *x y*, is shown in Figs. 55 and 56. The line *z* is the point of union of the two cell elements. The diaphragm chest (Fig. 57) obtained in this way contains, therefore, cells, which, considered from the middle line *r s*, are open above on one side and closed above on the other. Then all the chambers *m* contain, for instance, anodes and all the chambers *n* cathodes; thus the gas escapes separated at both sides of the apparatus. By this arrangement of the diaphragm chest, Garuti reaches a simplification of the points of contact compared to his older construction.

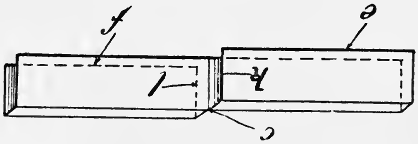

Fig. 53.

Fig. 54.

All insulating parts are of asbestos, which is not attacked by the dilute caustic soda solution. Lead and zinc soldering is to be avoided.

The partitions project below the electrodes at their under edges, but sufficient space is left between them and the bottom of the apparatus for accumulation of impurities from the electrolyte. The separation of the gas is thus made perfect. Since the electrolyzer is closed, the electrolyte absorbs no carbon dioxide from the atmosphere. The gas chambers have undergone no particular changes except the use of the water-gauge in connection with them. The hydraulic seal for the gas exit tubes is retained. The apparatus normally works with 200 to 400 amperes.

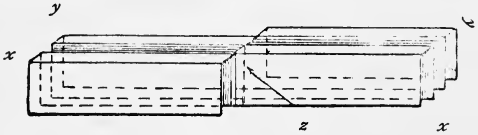

Fig. 55.

Fig. 56.

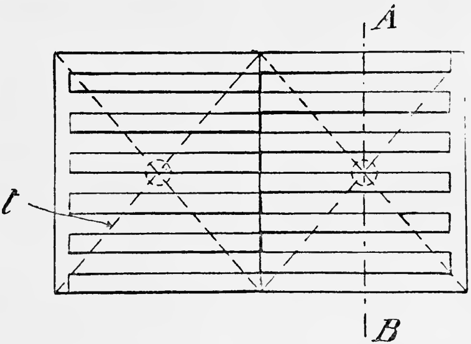

Fig. 57.

Figs. 58 and 59 show the most recent practical apparatus of Garuti's taken from a treatise of Buffa[1], who gave a lecture on this subject before the Association des Ingénieurs Electriciens in Luttich.

Del Proposto, the clever originator of the Garuti idea, also constructed an improvement, the arrangement consisting of four thin steel sheets rolled up into a spiral and separated from

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[1] Bulletin de l'Assoc. des Ing. Electr., **11**, 305 (1900). Nernst-Borchers Jahrbuch der Elektrochemie, **VII**, 338 (1901).

each other by insulating rods; two of the spirals serve as electrodes and two as diaphragms.

OPERATION.

Concerning the operation of the Garuti apparatus, we can, in general, repeat the information of the Schmidt publication exactly as on the former pages. We can add to this the information given by Buffa as follows:

The gases are led to the gasometers through iron tubes containing insulating sections of rubber. The enlargement in the vertical tube coming from the apparatus shown in Fig. 58 keeps back foam and spray of the electrolyte. The same drawing also shows the hydraulic seal which prevents the mixture of the gases in the electrolyzer by stopping any

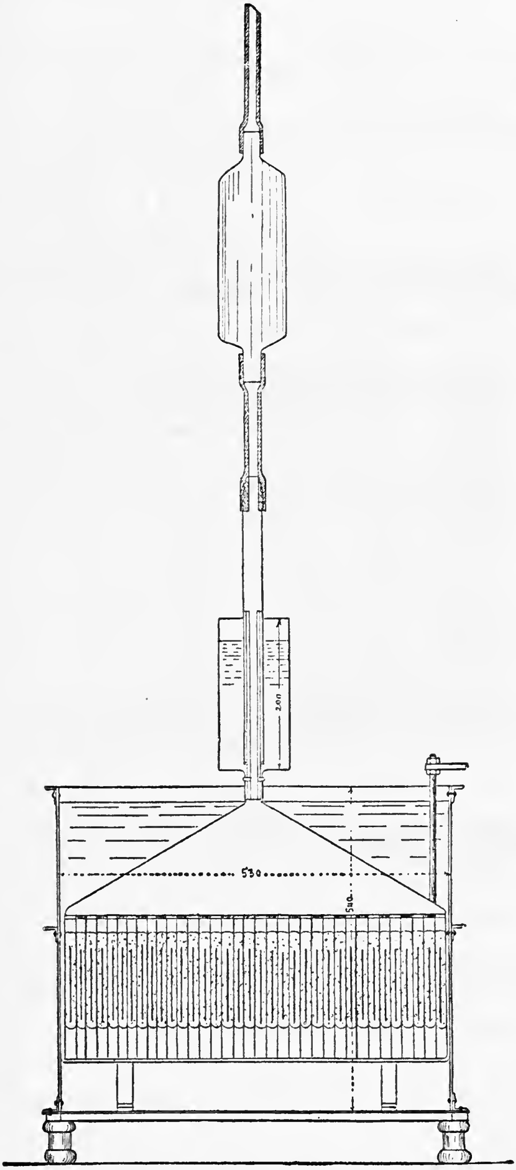

Fig. 58.

increase of gas pressure in the apparatus. After the gases have remained some time in the gasometers, in order to condense the water vapor, they pass to the compressors. Garuti lubricates the compression cylinder used for oxygen with water, since the compressed oxygen will ignite the lubricating oil with an explosion.

Also in the Garuti apparatus are to be found safety appliances in order to indicate at once any mixture of gases in the electrolyzer. As in the Schmidt apparatus two feeble currents of gas are led off and conducted over a piece of platinum sponge. As long as the gases were pure they burned with a quiet flame. The occurrence of small explosions and the extinguishing of the safety flame shows admixture of the gases. Naturally water flasks and safety wire meshes are used to prevent the explosions from striking back into the interior of the electrolyzer.

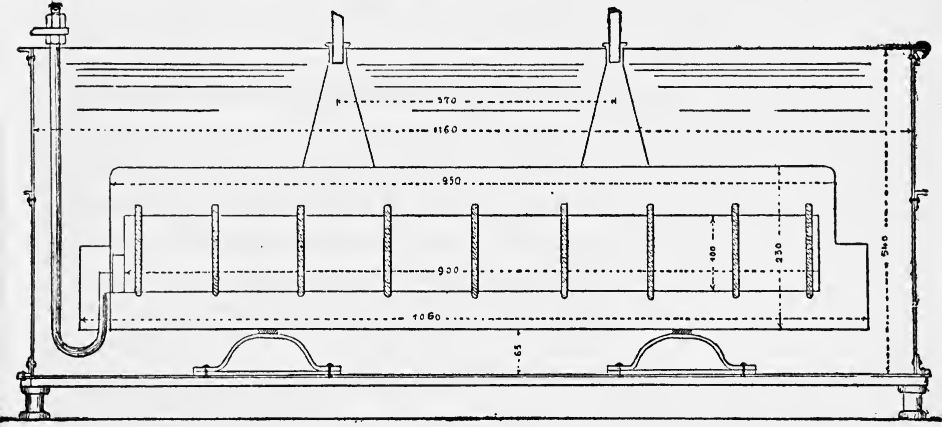

Fig. 59.

The usual accessories of a Garuti plant consist of the usual manometer tubes, a control voltmeter for the baths and the distribution pipes for the water.

PURITY OF THE GASES.

According to Buffa, the Garuti apparatus furnishes hydrogen 98.9 per cent. pure by chemical analysis, to 98.5 per cent. pure, according to their specific gravity. The oxygen is 97 per cent. If purer gases are desired they can naturally be prepared in the same way as was described in the Schmidt apparatus, *i. e.*, by passing them through red-hot tubes or other substances which cause combination by catalysis.

In the Garuti apparatus the purity of the hydrogen is usually not determined by chemical analysis but by the densimeter constructed by Bassani.

This instrument, according to Buffa,[1] is based on the law of Graham, according to which the exit velocity of a gas through an opening is inversely proportional to the square root of its density.

In the Bassani densimeter a determined quantity of gas is collected in a movable bell and allowed to escape through a small hole. As the gas escapes, the level of mercury which surrounds the bell and into which the latter dips, changes. The beginning and the end of the escape of gas is determined electrically by a second counter which gives exactly the duration of the outflow. The influence of temperature and atmospheric pressure are allowed for by suitable arrangements.

COST OF OPERATION.

Winssinger[2] gave, in 1898, some data on the cost of operating the Garuti apparatus. According to this a plant in operation in Brussels, produced 0.4 litre of hydrogen and 0.2 litre of oxygen per ampere hour. A normal apparatus of 350 amperes and 2.5 volts produced per twenty-four hours 1.68 cubic metres of oxygen and 3.36 cubic metres of hydrogen. The quantity of energy required daily is, therefore, 21,000 watt-hours, wherewith altogether 5.04 cubic metres of the two gases were obtained. The average consumption of energy is, therefore, 4,166 watt-hours per cubic metre of the

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[1] Bull. de l'Assoc. des Ing. Electr., 1900, **11**, 305; Nernst-Borchers: Jahrbuch der Electrochemie, **VII**, 341.

[2] Chem. Ztg., **22**, 609 (1898).

two gases. Buffa in the lecture previously alluded to repeated these figures as representing present practice. The current output is, therefore, in this apparatus about 96 per cent., and the energy output 57 per cent.

If we calculate the energy used upon only one of the two gases, for in making gas the obtaining of only one of the gases is sometimes the purpose of the operation, we will find an energy requirement of 12,500 watt-hours per cubic metre of oxygen and 6,250 watt-hours per cubic metre of hydrogen.

The required voltage varies according to the concentration of the electrolyte and is, according to Buffa, for

Water acidulated with sulphuric acid	3.00 volts
Caustic soda solution 21° Beaumé	2.45 "
Caustic potash solution 16° Beaumé	2.55 "
Caustic potash solution 18.5° Beaumé	2.45 "

With power costing ¼–1¼ cents per kilowatt-hour the cost of power figures out to be for

1 cubic metre of oxygen	3.1250–15.6250 cents
1 cubic metre of hydrogen	1.5625– 7.8125 "
1 cubic metre of detonating gas	1.0400– 5.2075 "

Sinking fund and interest on the plant, patent royalties, labor and consumption of electrodes are naturally not included in the above figures.

In a plant set up in Rome, the power cost $19.82 per kilowatt-year. This corresponds approximately to ¼ cent per kilowatt-hour. At this price of power the total operating cost for 1½ cubic metres of mixed gas is calculated by Buffa at 4 cents, not including sinking fund and interest. This amounts to, then, according to which gas is used, a cost for

1 cubic metre of oxygen	8 cents
1 cubic metre of hydrogen	4 "
1 cubic metre of detonating gas	2.65 cents

Interest and sinking fund will raise these figures to the following:

1 cubic metre of oxygen	15 cents
1 cubic metre of hydrogen	7.5 "
1 cubic metre of detonating gas	5 "

The compression of the gases would increase the cost of operation to the following:

1 cubic metre of oxygen	17 cents
1 cubic metre of hydrogen	8.5 "
1 cubic metre of detonating gas	5.65 cents

This small increase of operating expenses, ascribable to compressing the gas, is so low that it cannot include sinking fund and interest on the supply of flasks necessary for containing the gas.

COST OF PLANT.

The cost of a 100 H. P. plant, including buildings, motor and dynamos, 51 cells, using each 400 amperes, 2 gasometers holding each 100 and 50 cubic metres respectively, is given by Buffa at $14,000, which figures are increased to $20,000, if it is necessary to transform the current and compress the gas. The first cost of the necessary flasks, however, is not included in the above estimate.

PRACTICE.

Plants using the Garuti system are in operation for various purposes in Rome, Tivoli, Terni, by the Société l'Oxyhydrique in Brussels, and the Sauerstoff- und Wasserstoffwerken in Luzern. Besides these the Société de Montbard, with the previously mentioned Brussels company, are erecting a plant in Montbard which will use over 60 H. P., and will produce, working twenty hours daily, 180 cubic metres of hydrogen and 90 cubic metres of oxygen. This combined company, with a capital of 1,000,000 francs, is named L'Oxhydrique francaise.

Fig. 60 shows a view of the Garuti water-decomposing plant, in Brussels, the picture being taken from the last publication of Schoop[1].

Schoop gives the following data about the plant of the Sauerstoff- und Wasserstoffwerken in Luzern[2].

The three-phase alternating current is taken from the elec-

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[1] M. U. Schoop : Die industrielle Elektrolyse des Wassers, 1901, 119.

[2] Idem, p. 122.

trical company at Rathhausen, at 1500 volts and transformed in a rotary converter to a direct current of 75 volts. There

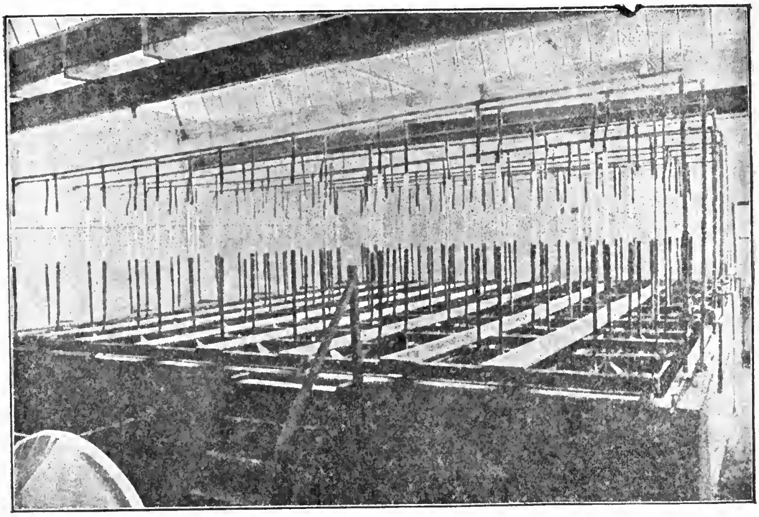

Fig. 60.

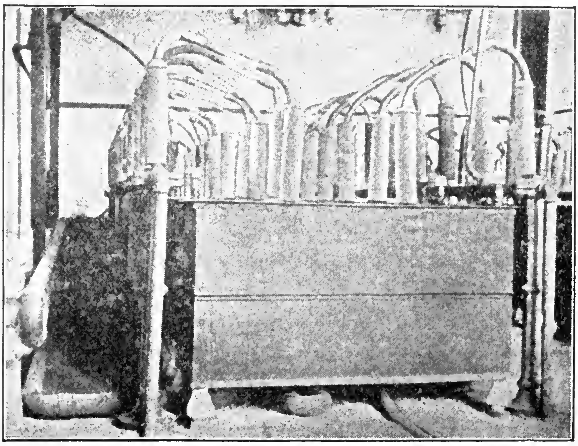

Fig. 61.

are 16 large and 32 small electrolyzers, which, in twenty-four hours, produce approximately 50 cubic metres of oxygen and

100 cubic metres of hydrogen. The corresponding gasometers contain 60 and 120 cubic metres respectively. The two compressors can compress 44 cubic metres of gas per hour.

The oxygen compressor was furnished by Thirion, of Paris, and can compress 8 cubic metres of oxygen per hour to 150 atmospheres, with a power consumption of 2.5 H. P. The hydrogen compressor, made by Schutz in Wurzen, requires 7 H. P. for an output of 36 cubic metres of hydrogen per hour, compressed to 200 atmospheres.

Fig. 61 shows a view of the electrolyzers used in Luzern.

A more detailed description of the plant in Rome is given by Buffa in the lecture already referred to[1] and the following is an exact reproduction from Borchers[2]. The plant is operated by Lieutenant Bossi and Captain Bassani. A diagrammatic sketch is shown in Fig. 62.

In this figure the parts are as follows: A main conductors (2000 volts), B automatic circuit breaker, C transformer, D safety fuse, E cut out, J automatic circuit breaker, L signal lamp, M asynchronous single-phase motor, P battery switch, R resistance, S rheostat, V voltmeter, *a* ammeter, *p* pole of the alternating current conductor, *q* pole of the direct current conductor, *r* direct current switch, *v* electrolyzing vessels.

The plant serves for the manufacture of hydrogen for the airship division of the Italian army, and has taken the place of the chemical hydrogen factory in which the gas was formerly made by the solution of iron in sulphuric acid. The gas obtained by the older method weighed 160 grammes per cubic metre, while pure hydrogen weighs 89 grammes per cubic metre.

The energy is furnished in the form of a 2000-volt (52-phase) alternating current by the electrical plant at Porta Pia, which itself receives this power from the Tivoli Falls, 27 kilometers (16 miles) distant. The primary current is then con-

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[1] Bull. de l'Assoc. des Ing. Electr., 11, 305 (1900).

[2] Nernst-Borchers: Jahrbuch der Elektrochemie, VII, 336 (1901).

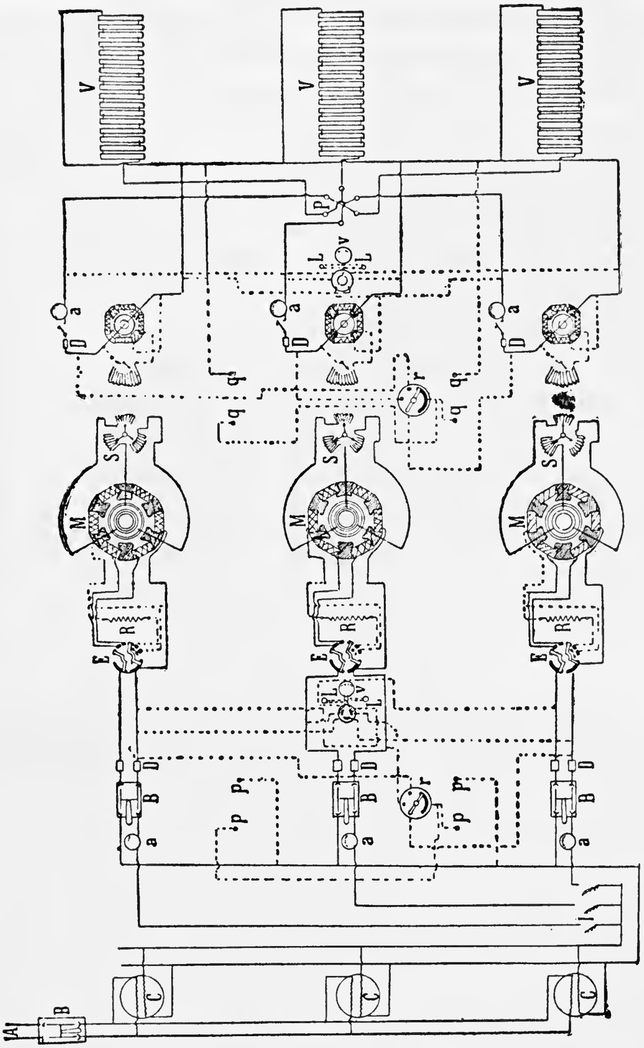


Fig. 62.

verted by means of three transformers, each of 30 kilowatt capacity. The secondary coils of the transformers run into a single conductor on one side, on the other side through three conductors in which automatic circuit breakers are inserted. The current is then taken from the switchboard to three single-phase, asynchronous motors, which are directly coupled to three 4-pole, direct-current dynamos (Thury system), each of 50 volts and of 400 amperes capacity. The common conductor leads from the negative poles of the dynamos to the electrolyzing cells, while the positive conductors of each dynamo pass to the switchboard upon which are measuring instruments, signal lamps, safety fuses, circuit breakers and switches. The latter are so arranged that each of the three dynamos can be connected with each of the three batteries of electrolyzers. There are 51 electrolyzing vessels divided into three groups. Each group of 17 cells is calculated for a current of 400–450 amperes, and require 45 to 50 volts. The electrolyzing vessels themselves are furnished by Garuti and Pompili of Rome. The arrangement of the apparatus is of the type shown in Figs. 58 and 59.

Process of Siemens Bros. and Obach, 1893.

In the group of apparatus with diaphragms of conducting material comes also the construction of Siemens Bros. & Co., and Obach, English patent 11,973/93 of the 21st of April, 1894.

FORM OF APPARATUS.

The apparatus shown in Fig 63 consists of a cast-iron vessel, *a*, surrounded with heat-retaining material. A porcelain support carries as anode, the iron cylinder, *f*, which is connected with the positive conductor through the iron rods *e e*. The cathode is formed of a second cylinder, *g*, which is connected with the negative pole by the connections *i i*. The electrodes are insulated by raising them upon the feet *r r*. The diaphragm is a metallic wire netting which is fastened to the hood *c* and separates the gases. The porcelain block *k* holds the wire netting fast in place. The electrolyte is dilute caustic soda solution. The gases escape by the tubes *m′* and *n′*, while the water used up is replaced through *O*. *p* is the water-guage. The level of the water must necessarily not

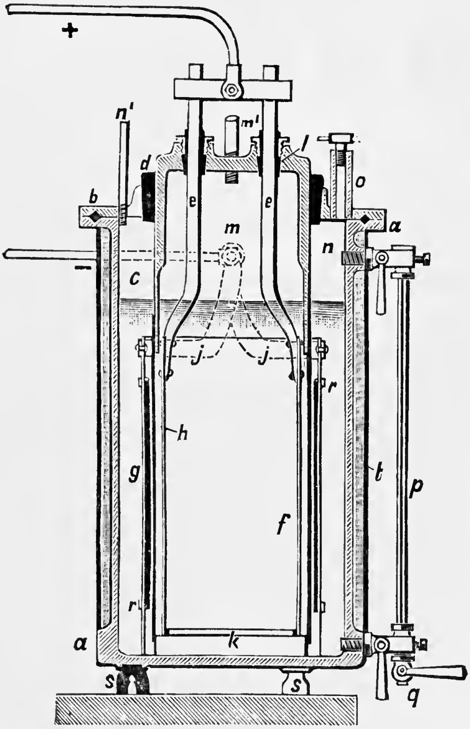


Fig. 63.

sink below the lower edge of the hood. The cock *q* serves for emptying the apparatus entirely when it needs to be cleaned. The whole apparatus is set upon insulated porcelain feet. The apparatus is recommended by its manufacturers as being of great durability, and very small resistance. The slight possibility of a mixture of the gases must not be forgotten, and in fact the degree of purity of the gas is given as 95 per cent., while other apparatus already described obtain a somewhat higher content.

In certain respects the apparatus may be taken for a modification which Garuti applied to his apparatus, for the use of the finely perforated strips in the sheet diaphragms by Garuti plainly underlies the idea on which the apparatus of Siemens Bros. & Obach is based.

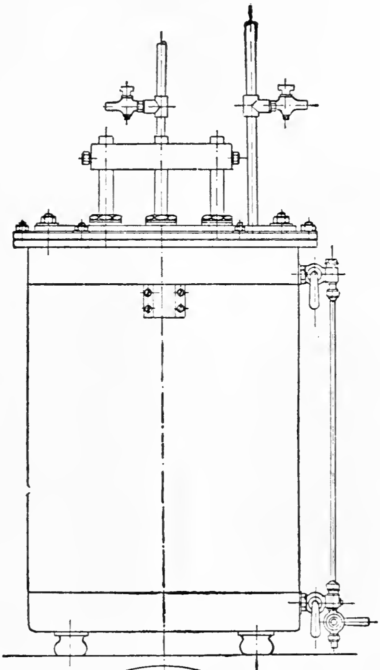
The exterior of a commercial Siemens Bros. & Obach apparatus is shown in Figs. 64 and 65.

The normal type of this apparatus is built for a current of 750 amperes at 3 volts.

OUTPUT.

Three such apparatus will furnish 11 cubic metres of oxygen and 22 cubic metres of hydrogen in twenty-four hours, requiring 162 kilowatt-hours.

Fig. 64.



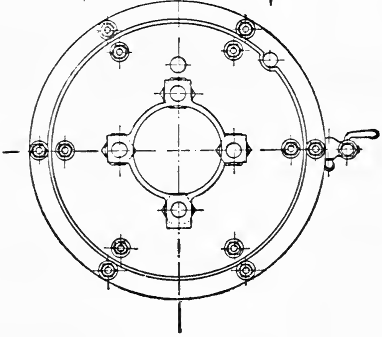


Fig. 65.

COST OF OPERATION AND PLANT.

The cost of power would therefore be, at the rates of ¼ and 1¼ cents per kilowatt-hour,

	¼ cent.	1¼ cents.
1 cubic metre of detonating gas	1.225	6.125
1 cubic metre of oxygen	3.675	18.375
1 cubic metre of hydrogen	1.850	9.250

The cost of such a plant with three electrolyzers is estimated as follows:

Three electrolyzers for 750 amperes each at 3 volts, including two connecting cables, one funnel, two run-off cocks, and two test cocks	$ 562.50
One dynamo 750 amperes, 9 volts, including a sliding base	650.00
Measuring instruments, switches, safety fuses, etc	75.00
Total	$1287.50

Not including motor, erection, electrical conductors, foundation work, as well as the piping for the carrying off of the gases from the electrolyzers.

Process of Schuckert, 1896.

As we have said on page 44, the apparatus of The Elektrizitäts–Akt.-Ges., formerly Schuckert & Co., belongs really to the arrangements with insulating partitions. We will describe it, however, in spite of this, in this class since it reminds one in several constructive details of the Garuti arrangement.

We cannot give a complete description of the Schuckert apparatus since it has not been patented, and the author must limit himself to the ideas which the firm in question have placed at his disposal without injuring their business interests. On the other hand the German provisional patent 80,504, of September 18th, 1896, gives some fundamental data.

According to this patent, The Elektrizitäts-Akt.-Ges., formerly Schuckert & Co., describe their patent as an "apparatus for the electrolytic manufacture of hydrogen and oxygen for industrial purposes, in which an insulating partition is interposed between each pair of unlike electrodes, and an insulating bell is placed over each electrode."

PATENT CLAIM.

The patent claim reads:

"An apparatus for the manufacture of oxygen and hydrogen by the electrolytic decomposition of caustic alkali solution, acids, or other suitable substances, without diaphragms, characterized thereby that the separate collection of the gases is obtained by:

1. Using between each pair of unlike electrodes an insulating partition composed of insulating material introduced through an opening in the side walls, therefore easily replaceable, and which does not dip so deeply into the fluid as the electrodes.

2. Bells of conducting or non-conducting material, lying upon the electrodes or insulated from them and dipping down as far as the middle of the electrodes."

After what has been said, the schematic sketch of the apparatus shown in Figs. 66–68 is easily understood without further description.

DESCRIPTION.

The apparatus consists of a cast-iron vessel[1] in which the corresponding number of bells are placed, which serve for catching the gases evolved at the electrodes, and with the exception of the copper conductors and the insulation, only iron is used in the construction of the apparatus.

The electrolyte is a 15 per cent. solution of sodium hydroxide in water. The water decomposed during the operation of the apparatus must be replaced by filling with distilled water as is practiced in accumulator batteries, in order that the solution retain its original concentration; the addition of sodium hydroxide is usually not necessary.

The apparatus can be connected up in series, each requiring 2.8 to 3 volts. The electrolyzers work best with an electromotive force of about 2.8 volts, if the electrolyte is kept at a temperature of about 70° C., which results without further provision simply through the heat developed by the current, if the electrolyzers are protected as far as possible from radiating their heat. To retain the heat in the apparatus they are surrounded by the non-conducting material which is the most easily obtained, as by placing them inside a wooden box slightly larger than the vessel, and filling the space in between with sand, so

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[1] Private communication from the author.

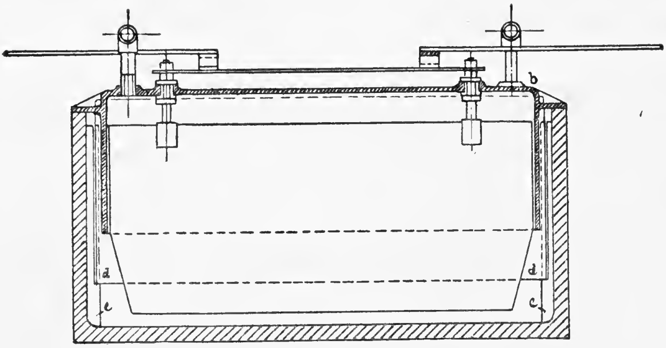

Fig 66.

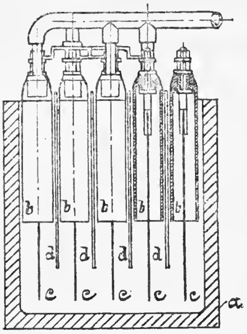

Fig. 67.

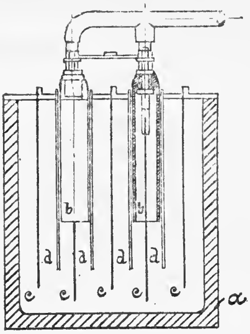

Fig. 68.

that the iron vessel is surrounded on the sides by a 5 cm. layer of sand. This arrangement renders the apparatus somewhat difficult of access.

MANAGEMENT.

At the start of the operation, the power required by the electrolyzer is more than the normal limit, since a certain amount of energy is necessary for heating the apparatus, that is for bringing the apparatus to the temperature at which it works best, *i. e.*, 70°C.

When it is possible to heat the above by means of steam to the normal working temperature, this extra expenditure of electrical energy is not required.

The gases evolved escape separately through iron nozzles to which are attached rubber hose in order to insulate the electrolyzers from the piping system. Then the gases pass through condensing chambers and washing apparatus to purify them from alkaline solution spray, and are then led to the gasometers.

The gases can be taken from the electrolyzers at a pressure up to about 60 mm. of water; above that pressure, mixing of the gases can take place in the apparatus. By observing this maximum pressure, the working of the apparatus is as has been shown in detail extremely safe, and the gases are obtained at 60 mm. water pressure of the purity of 97–98 per cent.

NORMAL TYPES.

The apparatus are built normally for a working current of 600 amperes, the cells being 660 mm. long, 450 mm. wide, and 360 mm. high, outside dimensions, and holding about 50 litres of solution. The weight of such an apparatus is about 220 kilograms.

OUTPUT.

Each apparatus produces, hourly, 220 litres of hydrogen and 110 litres of oxygen measured over water at 760 mm. mercury pressure and at 15° C.

The evolution of the gas takes place continuously. The gases are perfectly safe from explosion on leaving the apparatus and their further handling will cause no danger from such as long as the piping system, and washing and purification apparatus, and the compressors are installed in a sufficiently business-like manner.

It is unnecessary to repeat here the cost of plant and operating of the Schuckert apparatus given in the older literature[1] since, in this respect, the author is enabled to give data from the latest standpoint, furnished by the firm building the apparatus.

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[1] Zeitschr. für Elektrochem., 1897–1898, 456; Jahrbuch für Elektrochem., 1899, 347; Hammerschmidt and Hess: Chem. Zeitung, **22**, 123 (1898); Elektrochem. Zeitschr., 1898–1899, 191. L'Ind. électro-chim., II, 30.

COST OF PLANT.

The cost of a plant for the production of 100 cubic metres of oxygen and 200 cubic metres of hydrogen in twenty-four hours amounts to:

40 electrolyzers for 600 amperes at $62.50	$2,500.00
Filling the baths with electrolyte, installation and foundations for the electrolyzers, piping, ventilation and lighting plant, erection	1,000.00
Building, 70 square metres of ground area	1,000.00
Total	$4,500.00

This estimate of cost contains only the purely electrolytic plant; the cost of storing and compression of the gas is not included therein.

COST OF OPERATION.

The cost of operating, according to the data given to the author, using ¼ and 1¼ cents as the limiting prices per kilowatt hour, is as follows:

68 kilowatt in the electrolyzing chambers	$ 4.08	$20.40
Renewing of the electrodes and electrolyte	0.90	0.90
Repair and maintenance of the interior arrangements in the cell room	0.85	0.85
Repair of the building	0.175	0.175
Wages of two workmen	2.125	2.125
Various general expenses	0.75	0.75
Sinking fund and interest 15 per cent	2.25	2.25
Total	$11.13	$27.45

The cost amounts, therefore, for a daily production of 300 cubic metres of mixed gas to the following:

1 cubic metre of mixed gas	1.36– 6.8 cents.
1 cubic metre of oxygen	4.08–20.4 "
1 cubic metre of hydrogen	2.04–10.2 "

The cost of operation without sinking fund and interest on the gasometers and their appendages and without general expenses amounts to:

1 cubic metre of detonating gas	3.71 – 9.15 cents.
1 cubic metre of oxygen	11.13 –27.45 "
1 cubic metre of hydrogen	5.565–13.725 "

The cost of the compression as figured by The Electrizitäts-

Akt.-Ges., formerly Schuckert & Co., is 5-6¼ cents per cubic metre of gas, in which, however, the interest and sinking fund on the large investment in steel flasks is not included.

PRACTICE.

According to the information furnished the author, there is only one plant in operation under the Schuckert patents, namely, at the platinum works of W. C. Heraeus, in Hanau. The plant is intended for a current of 200 amperes at 30 volts, and furnishes 4 cubic metres of oxygen in ten working hours. A second plant, producing 1 cubic metre of oxygen per day, is said to have been erected in Berlin, but is no longer in operation.

B. Processes and Apparatus for the Electrolysis of Water without Separation of the Gas (Production of Detonating Gas).

(*a*) For Purposes of Instruction and Laboratory Work (Voltameter).

GENERAL.

In this group belong a part of the electrical measuring instruments which depend on the chemical action of the current. The determination of the strength of an electric current can be made by measuring or weighing the amount of detonating gas developed in an interval of time, quite as well as from the weight of precipitated copper or silver.

As in the industrial decomposing apparatus, so also in the mixed gas voltameter, either acid or alkaline solution may be used. In general, voltameters with alkaline electrolytes are preferred, since in using sulphuric acid inaccurate values are obtained by the production of ozone and persulphuric acid. The acid electrolyte used is, as a rule, 30 per cent. sulphuric acid, corresponding to a specific gravity of 1.3; for more accurate determinations, a solution of phosphoric acid is to be preferred. The alkaline electrolyte is, as a rule, a 15 per cent. solution of caustic soda free from chlorine.

The mixed gas voltameters are especially suited for calibrating instruments, and less suited as direct indicators of the amperage of the current. In this respect their construction of simple materials possesses a great advantage. As compared with the silver and copper voltameters they have the advantage of easier and simpler manipulation, and the disadvantage of less accuracy. H. A. Naber[1] has recently advised the use of the hydrogen voltameter.

REDUCTION OF GAS VOLUMES.

If the measurement is made by the determination of the quantity of evolved mixed gas, the volume read off must be reduced to 0° C. and 760 mm. barometric pressure. For this purpose the formula

$$v = v_1 \frac{(b - h)273}{760(273 + t)}$$

is used, in which v_1 indicates the gas volume read off, b the barometric pressure during the experiment, h the tension of water vapor at the temperature t of the electrolyte and gas. In using this formula, care must be taken that when the reading is taken, the level of the fluid in the gas tube and in the principal water receiver stands at the same height, which can be easily obtained by a careful raising of the tube in the vessel.

In determining the strength of the current, the reduced gas volume must be calculated for one minute's duration of experiment which is then divided by 10.44, the number of cubic centimetres of mixed gas evolved by 1 ampere in one minute.

When using acid electrolytes it is preferred to measure only the hydrogen in order to exclude, as far as possible, the influence of secondary reactions at the anode; then the volume read off and reduced by the use of the above formula must be increased 50 per cent. before dividing by 10.44.

At the end of this monograph is an appendix in which are given tables for the reduction of gas volumes to 760 mm.

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[1] "Standard Methods, etc.," by H. A. Naber and George Tacker, Salisbury, Court Fleet Street, London. H. A. Naber: "Das Wasserstoffvoltameter und seine Zuverlässigkeit," Elektrochem. Zeitscher. 1898–99, 45.

barometric pressure and 0° C., and also for the tension of water vapor in millimeters of mercury, in the range of ordinary temperatures at which experiments are made.

CONNECTIONS FOR CALIBRATION OF APPARATUS.

The connections used when calibrating with the voltameter are shown in Fig. 69, in which *S* is the source of current consisting of batteries or accumulators connected for tension. The electromotive force of the battery should be five or six times larger than is necessary to decompose water. This has the object of diminishing, as far as possible, the fluctuations in the current after closing the circuit, which may be so large as to make readings of the average value somewhat difficult when using small tensions. This irregularity at the start lasts so much the longer, the smaller the electromotive force of the battery used and the current density at the electrodes. The mixed gas voltameter is therefore preferable for the measurement of small currents, while the silver and copper voltameter is preferable for large currents. In Fig. 69, *V* is the voltameter, *G* the instrument to be calibrated, *R* an adjustable resistance, and *c* a switch.

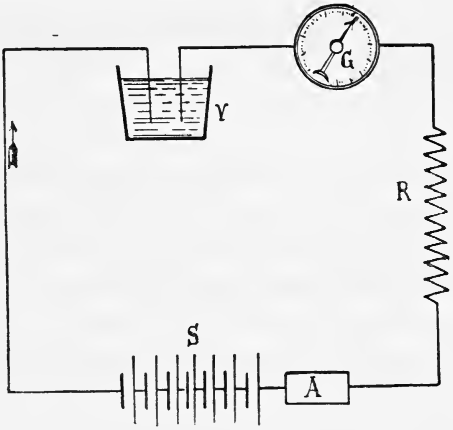

Fig. 69.

The accuracy of the measurement is dependent upon the accuracy of the reading off of the gas volume and is on the verage about 0.2–0.3 per cent.

Fig. 70.

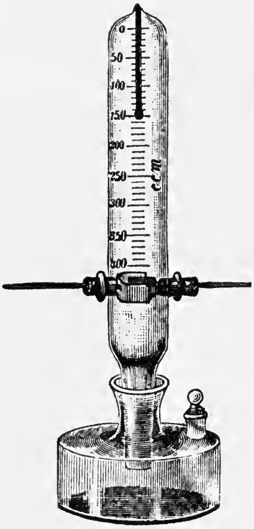

Fig. 71.

SIMPLE FORMS OF APPARATUS.

Fig. 70[1] shows a mixed gas voltameter of the simplest type. It consists of a cylindrical vessel filled with dilute acid, into which dips a graduated tube closed above. The tube is likewise filled with the electrolyte before the experiment. Inside the tube at the bottom are two platinum electrodes connected with the external circuit by two insulated wires.

VOLTAMETER OF KOHLRAUSCH.

A simple form for a current of about 30 amperes was proposed by Kohlrausch.[2]

The apparatus shown in Fig. 71 is made by the firm of Hartmann & Braun, in Frankfurt. It consists of a glass tube 40 mm. in diameter, graduated in centimeters and with its lower

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[1] Holzt: Die Schule des Elektrotechnikers, I, 102.

[2] Idem, I, 104.

extension ground into the neck of the large vessel. A thermometer is sealed into the measuring tube and renders possible an exact determination of the temperature. The platinum electrodes are introduced through the rubber stoppers, provided by means of the two side connections.

VOLTAMETER OF DE LA RIVE.

A simple voltameter which has the advantage that after the evolution of gas it is only necessary to invert the vessel with the firmly attached glass tube in order to refill it with dilute acid, is shown in Fig. 72. This apparatus, designed by De la Rive, allows in this form the catching of either one of the gases.[1]

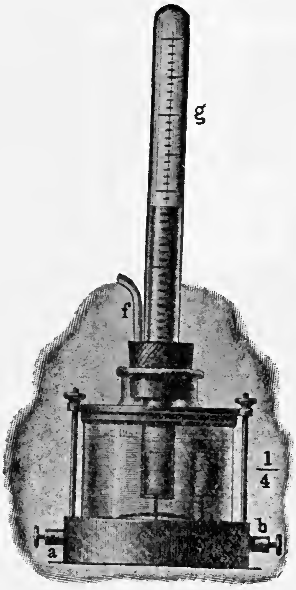

Fig. 72.

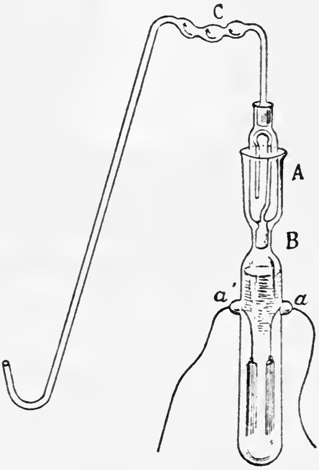

Fig. 73.

VOLTAMETER OF BUNSEN.

Bunsen[2] used for exact measurements a voltameter consist-

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[1] Wiedemann: Die Lehre von der Elektrizität, II, 477 (1894). Bertin: Nouv. Opusc. Mém. de la société mat. de Strasbourg, 6, 31 (1865).

[2] Pogg. Ann., 1854, 620.

ing of a glass flask (Fig. 73), in which the platinum wires leading to the electrodes were sealed at *a a'* and having the movable parts all ground in. The flask carries at *B* a drying tube, *A*, which, as well as the enlargement *C*, is filled with concentrated sulphuric acid, in case the mixed gas is to be collected in the dry condition over mercury. The tube carrying off the gas is likewise connected to the drying tube. For determinations by weight, the little flask carries besides this on one side a neck closed by a glass stopper, through which, after the close of the experiment, the mixed gas in the interior of the apparatus may be replaced by atmospheric air. Bunsen also recommends the keeping of the apparatus at a temperature of 60° by means of a water-bath and the use of very dilute sulphuric acid in order to prevent the formation of persulphuric acid, hydrogen peroxide, and ozone. Besides this, Bunsen especially recommends the replacement of the sulphuric acid by phosphoric acid.

VOLTAMETER OF OETTEL.

Oettel's voltameter enjoys an extensive use[1]. This, as seen in Fig. 74, consists of a thick-walled, cylindrical, glass vessel in which is arranged two cylindrical, concentric, sheet-nickel electrodes, immersed in a 15 per cent. caustic soda solution free from chlorine. The vessel is about 14 cm. high and about 6 cm. in diameter and closed air-tight by a rubber stopper. To avoid short circuits between the two concentric electrodes, a straight-walled, crystallizing cup is placed in the bottom with its walls between the two electrodes. This alkaline voltameter requires only a very low tension to operate it, in consequence of the very large electrode surfaces close to each other.

The instrument was first described by Elbs and Schonherr[2] who used it upon the advice of Oettel in their work upon the formation of persulphuric acid. At that time Oettel used a rectangular glass trough with three electrodes, *i. e.*, one anode

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[1] R. Lorenz: Elektrochemisches Praktikum, 1901, 13.

[2] Elbs & Schönherr: Studien über die Bildung von Uberschwefelsäure. Zeitschr. für Elektrochem., 1894–1895, 469.

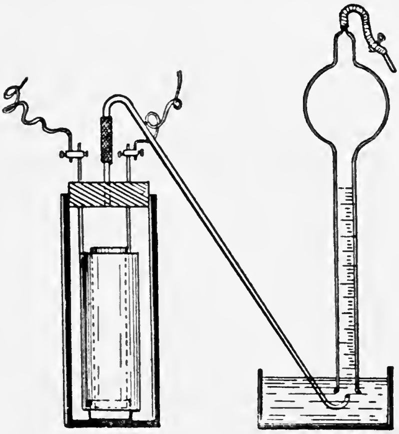

Fig. 74.

and two cathodes. The anode has a double surface of about 80 sq. cm., the cathodes a somewhat greater surface on the one side.

The experimenters write as follows concerning their investigations with this Oettel voltameter when using alkaline solution.

" The alkaline voltameter furnishes mixed gas free from ozone. Even with a current of 3 amperes the instrument warmed up only very slightly, while in the acid voltameter with this current the temperature rose quickly to 50° C. If the acid voltameter, as is the case in many constructions, possesses a small space for containing the sulphuric acid, the latter enriches itself after being used for a short time in consequence of the loss of water (partly also by the decomposition of water), and soon reaches such a concentration that the formation of persulphuric acid commences. This produces, naturally, a corresponding loss in oxygen; the sulphuric acid formed goes over to the cathode and is there reduced so that a loss of hydrogen also results. The amount of gas evolved will in consequence be considerably less than the quantity required by Faraday's law, if the filling up with water is not attended to carefully and at the proper time. An experiment confirmed this completely. If the acid voltameter is filled with acid of 1.4 specific gravity, and is connected at the same time with an Oettel instrument in the same circuit there will be obtained in the former, with a current strength of ½ ampere, 93.9 per cent. of the gas obtained in the latter; with 1 ampere 89.4 per cent., with 2 amperes 87 per cent., 3 amperes at first 87 per cent. then 90.8 per cent., and still later 93.6 per cent. The rise of the percentage with the last current strength is explained by the rise of the temperature of the voltameter to a condition of equilibrium in the last case and at high temperatures the formation of persulphuric acid diminishes. Using the acid of specific gravity of 1.15, the acid voltameter gave very accurate results. The test was made by a current of 3 amperes corresponding to a current density of 4 amperes per sq. cm.

The above averages are shown in the following table:

TABLE VI.

Current strength.	Tension.	Current density per sq. cm.	Remarks.
0.2 amperes	1.85 volts	0.25 amperes	The ordinary voltameter filled with sulphuric acid (with an anode surface of 7 sq. cm.) required on the other hand 3 to 3.5 volts tension.
0.5 "	1.98 "	0.62 "	
0.92 "	2.09 "	1.15 "	
2.42 "	2.32 "	3.02 "	
4.21 "	2.55 "	5.26 "	

VOLTAMETER OF WALTER-NEUMANN.

The voltameter of Walter-Neumann (Fig. 75) consists of a glass bulb, to which is attached a graduated glass tube with a glass stop-cock and funnel. The bulb contains the two platinum electrodes, which are connected with the source of current by platinum wires sealed through its sides. A rubber connecting tube communicates with the straight, ungraduated, glass tube carried by the same stand.

In using the instrument the filling tube is raised with the stop-cock of the graduated tube left open until the acidulated water fills the latter, upon which the stop-cock is closed and the current turned on. Working in this way, the irregular interval at the beginning of electrolysis falls within the time

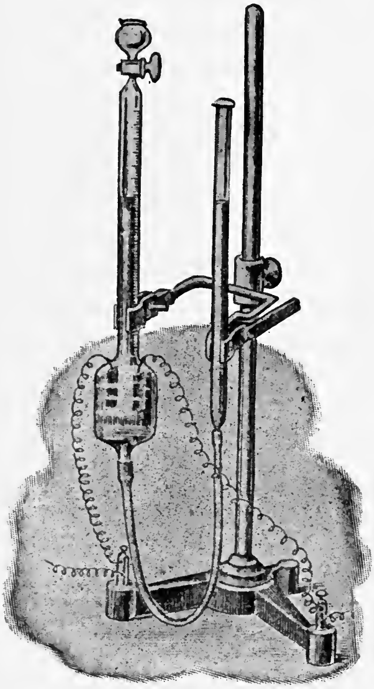

Fig. 75.

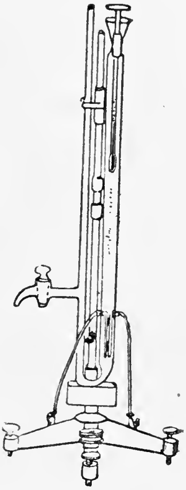

Fig. 76.

of the experiment. More accurate results are obtained if the filling tube is left with stop-cock open until the electrolyte in the graduated tube stands at the upper ° point, and the current then be turned on, the cock being still open, and the latter only closed when the current has reached a constant value, and the time of the experiment reckoned from this instant. During the electrolysis the filling tube is constantly lowered so that the level of the liquid in the graduated tube and the filling tubes are at the same height at the end of the experiment for the purpose of making the reading. The two glass tubes should be of nearly the same section in order to equalize the effect of capillarity, which is scarcely noticeable except in too narrow tubes.

Fig. 76 shows a voltameter on the same principle. It is distinguished by having the funnel closed by a ground stopper carrying a thermometer, and the leveling of the fluid in the two tubes is made, not by lowering the filling tube but by drawing off the electrolyte. The support carries an adjustable mark for indicating the level. It is not possible with this apparatus to equalize irregularities at the beginning of the electrolysis.

VOLTAMETER OF BERTIN.

The voltameter of Bertin employs the hydrogen alone for the measurement. It consists of a graduated burette, connected at its upper end by a capillary tube with a glass bulb. The latter carries a hose connection in order to be able to draw electrolyte into the burette. The burette dips into a vessel which contains the two platinum electrodes, of which only the negative one reaches into the burette. The capillary tube hinders the rise of gas bubbles into the gas bulb, so that the evolved hydrogen can be read off directly. The equalizing of the level of the liquids is done by the proper immersion of the burette. As far as concerns the irregularities at the beginning of the experiment, the same suggestions apply to this as to the previous arrangements.

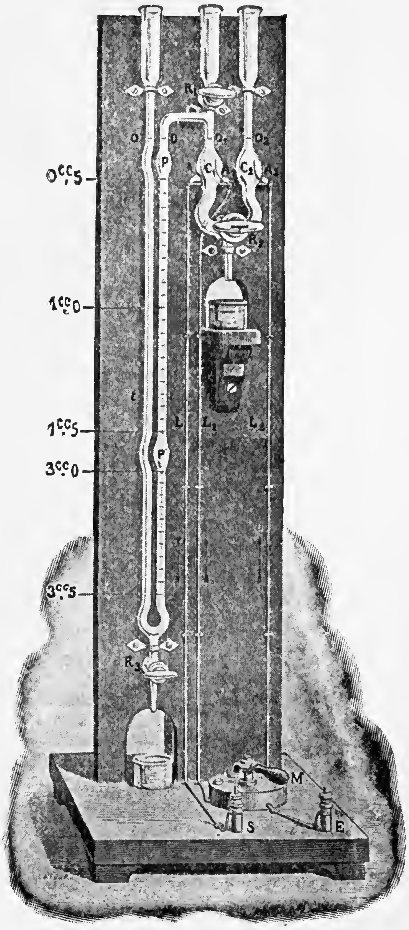

Fig. 77.

VOLTAMETER OF MINET.

Two voltameter constructions of Minet[1] are different from those already described. One arrangement, which is shown in Figs. 77–80, is intended to avoid the sources of error in the mixed gas voltameter, such as absorption of gas and secondary reactions.

The apparatus consists of two principal parts. In the upper right-hand part are two decomposing vessels, C_1C_2, which communicate with each other by the three-way stop-cock R_2. To the left are two communicating tubes. The tube t is graduated and is in combination with the decomposing space C_1, by means of the narrow, bent tube O O_1. The electrolyte is poured in through the filling tube connected with the decomposing vessel C_2, in charging which the stop-cock R_2 has the position shown in Fig. 78 and the stop-cock R_1, is left open. The electrolyte is run in to the marks O_1 O_2. Then the tubes tt^1 are filled to the marks O O^1, during which the the stop-cock R_1 is left open and R_3 is closed. The latter has the object of exact adjustment of the level in the communicating tubes.

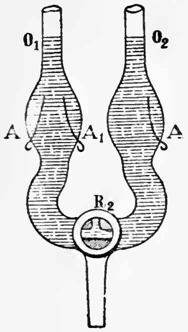

Fig. 78.

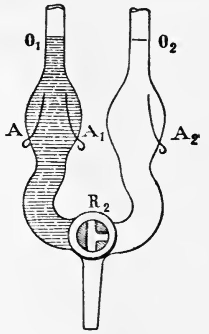

Fig. 79.

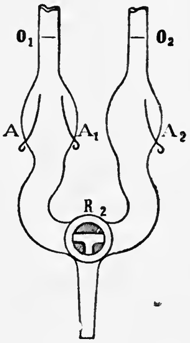

Fig. 80.

At the beginning of the electrolysis the electrolyte must be exactly adjusted to the marks O^1 O O_1 O_2. Fig. 80 shows the position of the three-way cock R_2 as soon as the electrolyte is to be replaced for another measurement.

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[1] Traité théorique et pratique d'Electro-Chimie, 1900, 353.

The decomposing vessel C_2 contains only one electrode A_2, while the decomposing space C_1 contains two of them A and A_1. This arrangement allows either mixed gas or oxygen or hydrogen to be caught as desired. The determination is only made when the current has become constant. This is quickly reached when the source of current has a sufficiently high electromotive force, and its strength is correspondingly regulated by a rheostat.

During the beginning of the electrolysis the stop-cock R_1 remains open. Closing the same is the beginning of the experiment, opening the switch is the end. The equalizing of the pressure in $t t^1$, necessary for reading the gas volume, is done by the manipulation of the dropping stopper R_3. The water used is saturated with oxygen and hydrogen before the experiment and is acidulated with 0.5 per cent. sulphuric acid.

According to Minet's researches, which are in part reproduced in the following table, the method of working described is suitable only for currents under 0.5 ampere.

TABLE VII.

Calibration of a galvanometer. Inner resistance at 18° C. = 17.1 Ohms.

Inserted resistance.	Current strength in the voltameter. J	Current strength in the galvanometer. i	Number of divisions. n	Galvanometer constant. $k = \frac{i}{n}$
Ohm.	Ampere.	Ampere.	—	Ampere.
∞	0.00369	0.00369	9.65	0.000382
"	0.00859	0.00859	22.50	0.000382
"	0.01464	0.01464	38.50	0.000380
4.00	0.07608	0.01415	37.00	0.000382
"	0.0997	0.01897	49.80	0.000381
"	0.1098	0.02097	55.00	0.000381
0.734	0.1197	0.00496	13.00	0.000381
"	0.1206	0.00498	13.00	0.000383
2.00	0.1206	0.01272	33.00	0.000385
0.734	0.1585	0.00656	17.00	0.000386
"	0.279	0.01155	30.00	0.000385
"	0.417	0.01722	45.00	0.000382
"	0.466	0.01925	50.00	0.000385
"	0.557	0.02296	60.00	0.000383

Minet claims for his apparatus the following:

(1) The decomposing spaces are independent of the rest of the apparatus. Their volume can be reduced at pleasure. The electrolyte is therefore quickly saturated with gas.

(2). If the pressure is kept constant during the experiment by manipulating the stop-cock R_3 there need be no fear that the volume read off will be too large by reason of the setting free of absorbed gas.

(3). The volume of the tube between O O_1, is so small that no correction is necessary for differences of temperature. .

(4). The graduated tube *t* consists of several parts: Of two enlargements (P P_1) of different content, and a straight tube which is divided in 0.01 ccm. The divisions are 2 mm. apart. The enlargements allow the measurement with the one apparatus of widely varying current strengths without giving to the graduated tube abnormal dimensions.

(5). Since *t* and *t'* are of like calibre, no correction is necessary because of capillarity.

Using electrolytes with 0.5 per cent. sulphuric acid and a current strength below 0.5 ampere, there is no loss by the formation of ozone, hydrogen dioxide, or persulphuric acid, as well as no loss of hydrogen noticeable by reduction of these products. These accessory phenomena only begin with a higher acid concentration and a greater current strength.

VOLTAMETER OF MINET FOR INDUSTRIAL PURPOSES.

Minet's voltameter for industrial purposes[1] rests on another principle of construction.

In this arrangement the increase of pressure upon an enclosed volume of gas is measured.

A glass vessel with a contraction *O*, as in Fig. 81, stands in combination with a manometer *M*, which is constructed to stand a pressure of two atmospheres and allows reading to 1/100 of an atmosphere. *A* is a tube which may be hermetically closed and through which the electrolyte may be poured in.

The lower compartment of the glass vessel contains the electrolyte, the level of which is raised at the commencement of each measurement to the mark *O* so that the upper part of the apparatus always contains the same gas volume *V*.

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[1] A. Minet: Traité théorique et pratique d'Electrochemie, 1900, 357.

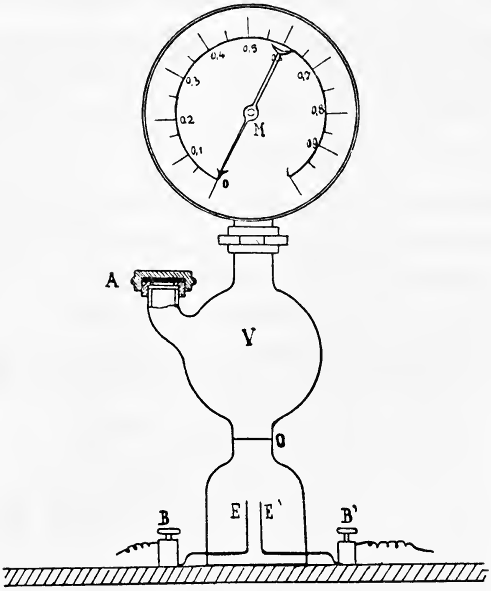

Fig. 81.

The increase of pressure shown by the manometer is

$$p = K_1 v \ldots\ldots\ldots\ldots\ldots\ldots (1),$$

in which v is the volume of the gas evolved during the measurement reduced to normal atmospheric pressure P; K_1 is a coefficient depending upon the volume V and the pressure P. Therefore we have

$$K_1 = \frac{P}{V}$$

and

$$p = \frac{P.v}{V}$$

on the assumption that the temperature during the experiment remains constant.

Since, on the other hand, the volume V of the gas evolved is proportional to the current strength Q, therefore

$$v = K_2.Q,$$

$$Q = \frac{1}{K_2}.v,$$

and putting for v its value from the first equation, we have

$$Q = \frac{p}{K_1 K_2},$$

and if we place $\frac{1}{K_1 K_2} = K$, we have $Q = K.p$; that is, the current strength going through the galvanometer is proportional to the pressure shown by the manometer.

The coefficients $K_1 K_2$ which limit the value K can be calculated if we know the pressure at the start, and the temperature, which is taken as constant for the duration of the experiment.

Usually the coefficient K is determined experimentally by a comparison of the manometer results with those of a correctly calibrated galvanometer, and correctly measuring the time of the electrolysis.

The voltameter naturally gives accurate readings only when the temperature and pressure are the same as when the instrument was calibrated. But since the temperature in laboratories varies very little and the atmospheric pressure seldom more than 1 per cent. above and below the normal, the instrument is sufficiently exact for a series of practical tests with small current strength; for example, for rough electro-analytical work where it can be used likewise as a current meter.

For a volume of V = 1500 ccm. and an allowable increase of pressure of 3 atmospheres, the instrument will register 4–5 ampere hours.

(*b*) For Technical Purposes.

Process of Eldridge, Clark and Blum, 1898.

For the technical manufacture of mixed gas (oxy-hydrogen gas) we know of only one, that of Eldridge, Clark and Blum, U. S. patent, 603,058.

We have not heard of the practical application of this proposal, and since such is hardly to be expected, it will suffice if we here, for the purpose of completeness, reproduce extracts from the patents which have appeared in the technical journals.[1]

The whole arrangement is shown in Figs. 82–84.

A steel cylinder, *2*, provided above and below with flanges, *5* and *6*, is lined inside as thickly as possible with a coating, *10*, of graphite or some difficultly fusible material. The bottom of the space inside is formed of the carbon cathode *13*, fastened tightly to the steel floor-plate *3*. The latter arrangement is held tightly down upon two stoneware plates, *8* and *9*, by bolts *7*. There are diametrically opposite openings, *11* and *12*, through the two walls of the cylinder, the first for leading in water and the last for discharging the gas formed. The inside of the cylinder is closed air-tight by a _||_ shaped cover made tight by an asbestos gasket, *18*, and screwed down by the bolts *17* to the flange *6*. The carbon anode *14* projects through the prolongation 19 of the cover, insulated by means of asbestos and loam. A metal cap, *20*, is screwed also upon the prolongation and likewise insulated by the mixture at *22* to *24*. The upper end of the anode is fastened in a clamp, *25–24′*, which runs on a rack, *27*. The latter is movable vertically by a spur-wheel, *31*, held in a frame, *28*, having on its

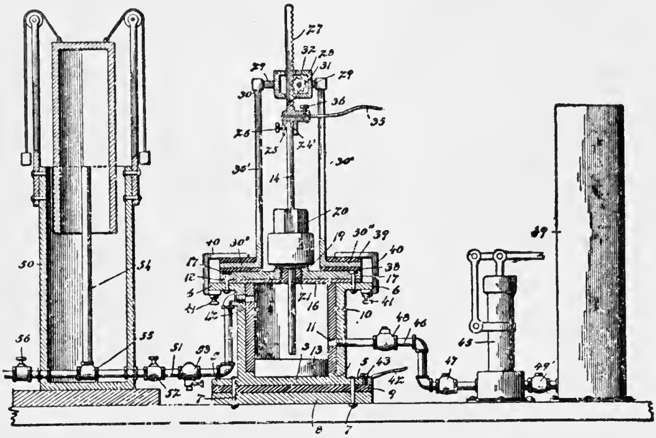

Fig. 82.

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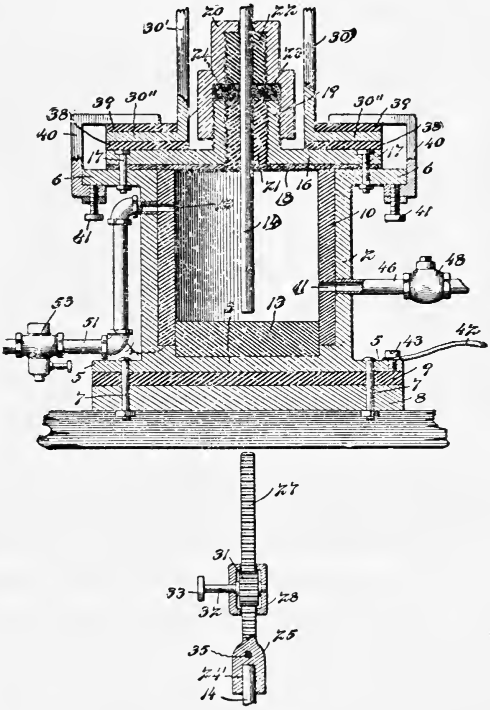
[1] Zeitschr. f. Elektrochem., 1898–1899, 246.

axle an insulated handle, *32*. The rack and the frame rests on a stand, *29–30′*, which is screwed down upon the flange *6* of the cylinder by means of the insulating rings *38*, *39* by two clamps, *40–41*. The electric current is introduced by the wires *35–42* held fast by the screws *36*, *43*. The electrodes are brought into contact with each other and after the formation of an arc, slightly separated. Then the pump *45* through the conductors *46–49′* forces water from the holder *49* through *11* into the interior of the cylinder where, in consequence of the heat from the arc, the water is decomposed and goes off as mixed gas through *12*. A part of the oxygen, however, combines with the carbon of the electrodes to form carbon dioxide. The gas mixture is led off to the gasometer *50* through the valves *53-56*. A large part of the carbon di-



Figs. 83 and 84.

oxide is there absorbed by waste water. The whole apparatus is so built that the single pieces (cylinder, gasometer, etc.) are easily taken apart and transportable.

C. Processes for the Simple Evolution of Oxygen.

(*a*) Through Depolarization at the Cathode.

Many have attempted to produce pure oxygen by the electrolysis of water without the use of diaphragms, by using depolarizing cathodes to absorb the hydrogen through a reducing reaction.

Process of Coehn, 1893.

Of these attempts, most attention has been given to that of Dr. A. Coehn, German patent 75,930, of the 14th of July, 1893.

PATENT CLAIM.

"An apparatus for the electrolytic production of oxygen and the halogens, characterized by the use of a cathode consisting of metal, and capable of absorbing hydrogen in order that the same may be used in a primary or secondary element for the generation of the electric current."

DESCRIPTION.

In wording this claim so generally, Coehn had especially in mind the use of negative accumulator plates as cathodes. These absorb, as they do in the ordinary charging of accumulators, the hydrogen set free at their surface up to a certain saturated point, which is recognized by the strong evolution of free hydrogen. These cathodes loaded with hydrogen are then to be used in a primary or secondary element as electrodes, whose make-up is adjusted to the local conditions. Coehn instances an element of the Daniell type, in which the Pb–H electrode replaces the zinc and is separated from the copper in the copper sulphate solution by a diaphragm. Coehn also proposes single fluid cells, such as Pb–H, against carbon or copper in sulphuric acid. Polarization is to be avoided by a rapid circulation of the sulphuric acid or by blowing in air. The work done by the current furnished by these elements is to partially supply the current necessary for the production of oxygen.

The apparatus has not found application in practice since it is indeed difficult to stick close to the border where the cathode plate shall be properly utilized and yet no hydrogen be evolved from it. One is also not sure of not obtaining an explosive gas mixture. Besides that, the partial recovery of the energy by the precipitation of copper out of copper sulphate in the Daniell cell would indeed be too expensive for technical purposes.

COPPER OXIDE CATHODES.

It is self-evident also that copper oxide cathodes may be used as depolarizers for the electrolytic obtaining of oxygen.

The property of the copper oxide cathode of being easily regenerated is an advantage, but such an arrangement has, however, the disadvantage, as against the Coehn proposition, of a small mechanical strength of the oxide plate, and the disagreeable work of handling concentrated alkaline solutions.

In the technical operation of the process thus briefly described, great difficulties are to be expected in the control of the operation, which obstacles will outweigh the attempted economy in energy.

Process of Habermann, 1892.

Habermann[1] studied likewise the different methods of obtaining oxygen by electrolysis. The occlusion of hydrogen by palladium demonstrated its in applicability for the manufacture of large quantities of oxygen. Better results were obtained with a solution of potassium permanganate acidulated with sulphuric acid. According to Habermann's results the use of a solution of potassium chromate acidulated with sulphuric acid is the most suitable. If the solution contains 20 per cent. potassium chromate, no evolution of hydrogen takes place. No probability of the tech-

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[1] Zeitschr. f. ang. Chemie, 1892, 323–328.

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nical utilization of this process can be entertained in view of the high price of the raw materials.

(*b*) By the Precipitation of Metal at the Cathode.

The obtaining of oxygen in the electrolytic way is possible by decomposing metallic oxide salts, using insoluble anodes and simply precipitating the metal out electrolytically. This metal must naturally be such as to be separated out in thick layers of precipitate with a good efficiency and without the formation of hydrogen or with very little of that gas. On this assumption quite a series of metals as zinc, nickel, etc., are used.

PRECIPITATION OF COPPER.

Copper fills the conditions the nearest, but when using this metal a very careful control of the operation is necessary in order to use up the electrolyte as far as possible, and on the other side the conditions in price between the metal precipitated and the metallic salt from which it is taken, works against the industrial application of the process; and finally, since the solution cannot be entirely freed from the metal and the saturation of the solution with oxide costs still more, there results a worthless dilute solution of the corresponding free acid in which the remainder of the metallic salt is still contained. Hoffer[1] recommends for laboratory purposes the electrolysis of copper sulphate solutions with insoluble anodes, producing oxygen. The electrodes are of different sizes; the current density at the cathode is as small as possible, at the anode as large as possible.

The industrial application of the methods mentioned in this group is not to be expected for the purpose of the manufacture of electrolytic oxygen.

Chronological Review.

Having now, on the previous pages, mentioned almost all of the electrolytic processes, some of which have only been pro-

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[1] Math.-naturw. Ber. aus Ungarn, Bd. 1 u. 2. — Ber. der deutschen chem. Ges., **22**, 168. — Die chemische Industrie, **12**, 200.

Number.	Date.	Name.	Patent.			Connection.
			Place.	Number.	Date.	
1	1885	D'Arsonval	—	—	—	Single pole
2	1888	D. Latchinoff	Germany	51998	Nov. 20, 1888	Single pole
			—	—	—	Double pole
3	1888	Ducretet	—	—	—	Single pole
4	1888	Renard	—	—	—	Single pole
5	1890	Delmard	Germany	52282	Nov. 23, 1890	Single pole
6	1892	Habermann	—	—	—	Single pole
7	1893	Dr. A. Coehn	Germany	75930	July 14, 1893	Single pole
8	1893	Bell	Germany	78146	Oct. 30, 1893	Single pole
9	1893	Garuti Garuti & Pompili Société l'Oxyhydrique	Germany England U. S. A.	83110 16588/93 534295	— Aug. 5, 1893 Feb. 19, 1895	Single pole
			Germany England U. S. A.	83097 23663/96 629070	— March 6, 1897 July 18, 1899	
			Germany England	106226 12950/900	Feb. 16, 1898 Oct. 24, 1900	
10	1893	Siemens Brothers & Co. and Obach	England	11973/93	April 21, 1894	Single pole
11	1894	E. Ascherl	Austria	44/5862	Sept. 26, 1894	Single pole
12	1896	El. A. G. formerly Schuckert & Co.	Germany	G. M.[1] 80504	Sept. 19, 1896	Single pole
13	1898	Hazard-Flamand	Germany	106499	June 12, 1898	Single pole
14	1898	Eldridge, Clarke and Blum	U. S. A.	603058	—	Single pole
15	1899	Dr. O. Schmidt	Germany	111131	June 13, 1899	Double pole
16	1899	P. J. F. Verney	France	280374	—	Single pole
17	1900	M. U. Schoop	Germany Austria	G. M.[1] 141049 1285	Sept. 5, 1900 1900	Single pole

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[1] Registered design.

Method of separation of the gases.	Separating material.	Electrodes.	Current density amperes per sq. cm.	Working electromotive force. Volts.	Electrolyte.	Products of decomposition	
						+	—
Porous diaphragm	Linen or cotton	Iron	2	?	30% KOH	O	H_2
Porous diaphragm	Asbestos cloth	Iron	3.5	2.5	10% NaOH	O	H_2
		+ Lead — Carbon			10–15% H_2SO_4		
	Parchment paper	Iron	10.0		10% NaOH		
Porous diaphragm	Asbestos cloth	Iron	?	?	Alkaline	O	H_2
Porous diaphragm	Asbestos cloth	Iron	?	2.7–3.0	13% NaOH	O	H_2
Porous diaphragm	Asbestos cloth	Iron	?	?	Alkaline	O	H_2
—	—	Platinum	?	?	20% K_2CrO_4 + H_2SO_4	O	—
—	—	Lead	?	?	H_2SO_4	O	—
Porous diaphragm	Asbestos cloth and vegetable fibres	Iron with granules	?	?	15% NaOH	O	H_2
Conducting partitions	Lead	Lead	2–4	2.45–3	12% H_2SO_4	O	H_2
	Sheet iron with a zone of perforations beneath	Iron	2		NaOH, 21° B. or KOH 16–18° B.		
	Sheet iron with a zone of perforations in the middle						
Conducting partitions	Iron wire netting	Iron	?	2.5	Alkaline	O	H_2
Impermeable bells	Glass	Silver or platinum wire	?	?	Dilute H_2SO_4	O	H_2
Impermeable partitions	Insulating material	Iron	?	2.8–3.0	15% NaOH	O	H_2
Non-conducting gutters	Non-conducting material	Metal	?	?	?	O	H_2
None	None	Carbon	?	Arc	Water	O +	H_2
Porous diaphragm	Asbestos cloth	Iron	About 2	2.5	10% K_2CO_3	O	H_2
Non-conducting gutters	Non-conducting material	Iron	?	?	NaOH	O	H_2
Impermeable tubes	Glass or clay	Iron	?	2.25	Alkaline	O	H_2
		Hard lead		3.6–3.9	H_2SO_4 D=1.235		

posed, others really introduced into practice, Table VIII (pages preceding) has been constructed for an easy review, in which the processes are arranged in chronological order, according to the time of their publication, together with the most important characteristics of each.

IV. APPLICATIONS.

General.

From the previous section and the applications which were described, it may be assumed that the question of the industrial electrolysis of water for the purpose of obtaining oxygen and hydrogen has been solved in numerous ways, regarded from the standpoint of technical construction. Also improvements in the apparatus and processes are necessarily not excluded, yet they will in no case hereafter be of such comprehensiveness as to affect the question of the applicability of the technical electrolysis of water. On the other hand, as Schmidt has opportunely remarked in one of his lectures, the applicability of such processes has become much more of a practical question for discussion since the recent developments in the line of cheap power, and the improvements which have been made, particularly in the carbon dioxide industry in the storage, compression, and transportation of gas.

There is left for us to describe separate installations of the processes of the above-mentioned apparatus, and their capability of competing with other processes.

Before passing to these we will bring together in compact form data of the cost of plant and cost of operation given in the description of the various processes.

COST OF PLANT.

(Only the cost of the electrolyzers is taken into consideration.)

From this presentation it is seen that the bipolar connected Schmidt apparatus costs more for plant, especially for small plants, than the single pole apparatus. In this connection it

TABLE IX.

(Cost of Plant for One Kilowatt of Energy Used.)

System.	Unit size of apparatus.			Price in dollars.	Price in dollars per kilowatt.
	Amperes.	Volts.	Kilowatts.		
Renard.	365	2.7	0.98	20.00	20.50
Schmidt.	15	65	0.975	440.00	451.25
	30	65	1.950	600.00	307.50
	60	65	3.900	800.00	205.00
	100	65	6.500	1100.00	169.25
	150	65	9.750	1800.00	182.00
	15	110	1.65	488.00	298.00
	30	110	3.30	700.00	212.00
	60	110	6.60	960.00	145.50
	100	110	11.00	1500.00	136.25
	150	110	16.50	2400.00	145.50
	15	220	3.30	750.00	227.25
	30	220	6.60	1062.50	161.00
	60	220	13.20	1825.00	135.75
	100	220	22.00	2680.00	121.75
	150	220	33.00	4300.00	130.25
Schoop.	175	3.6	0.63	69.25	109.75
Garuti.	400	2.5	1.00	?	?
Siemens Bros. and Co. and Obach.	750	3.0	2.25	187.50	83.25
El. A. G., formerly Schuckert and Co.	600	2.9	1.74	62.50	36.00

must not be overlooked that with bipolar connections a considerable amount will be saved in piping, electrical conductors, and erection. This difference is most easily seen when we consider, for instance, the operation of the plant for the filling of air balloons. A normal military balloon requires, in order to be filled in twenty-four hours, a plant of about 200 kilowatts. To do this, 6 or 7 units of the Schmidt apparatus of the largest type will be necessary, while 320 of the Schoop electrolyzers, 200 of the Garuti, 90 of the Siemens Brothers & Obach, and 115 of the Schuckert system will be required. We have left out the small differences in the operating voltage, since we wish to make only a rough approximation.

Further, in making an approximation of the cost of plant we must take into consideration the fact that except when very large plants are to be erected in which a sufficient number of anodes can be placed in series, and connected to an ordinary lighting circuit, the single pole apparatus otherwise requires the installation of a particular kind of low voltage and relatively expensive dynamo machine with all its accessories.

COST OF OPERATION.

The following costs of operation have already been given for the various processes used in industrial practice, conclusions being made on the assumption of either one of the two or the mixed gases being utilized.

Along with the cost of production several other factors may be thought of, which, under some conditions, would add materially to the cost of operation.

CONSUMPTION OF ANODES.

One question would be the using up of anodes when working with iron electrodes in alkaline solutions. The view of most of the constructors of electrolytic apparatus for the decomposition of water that the corrosion of the electrodes may be practically neglected because of the "passive condition" of the iron, appears not to be completely substantiated. This question was discussed in connection with the presentation of the Schmidt apparatus at the seventh yearly Assembly of the German Electrochemical Society of Zurich. According to the communication which Heraeus has made upon the basis of the operation of his Schuckert plant, the consumption of anodes is not unimportant. Heraeus supposed the cause to be primarily in the presence of chlorine and sulphuric acid in the cheap caustic soda solution, and replaced the same by the purer and more costly caustic potash, without, however, diminishing the consumption of the iron electrodes. The electrodes lasted in the latter case as in the former about one year. The

TABLE X.

Cost of Producing the Gases per Cubic Meter.

System.	Mixed gas.		Hydrogen.		Oxygen.		Remarks.
	Power costing		Power costing		Power costing		
	¼ c. per kilowatt hour. Cents.	1¼ c. per kilowatt hour. Cents.	¼ c. per kilowatt hour. Cents.	1¼ c. per kilowatt hour. Cents.	¼ c. per kilowatt hour. Cents.	1¼ c. per kilowatt hour. Cents.	
A. *Pure cost of power for the electrolysis without compression.*							
1. Schmidt	1.000	5.000	1.500	7.500	3.000	15.000	
2. Schoop:							
(*a*) alkaline	0.900	4.500	1.325	6.750	2.750	13.500	
(*b*) acid	1.540	7.750	2.325	1.150	4.500	23.250	
3. Garuti	1.050	5.250	1.540	7.750	3.000	15.500	
4. Siemens & Obach	1.225	6.000	1.850	9.250	3.675	18.375	
5. Schuckert	1.325	6.750	2 025	1.025	4.075	20.400	
B. *Total cost of production including sinking fund and interest, but without compression.*							
1. Schmidt	7.775	13.250	11.250	19.250	22.000	38.000	
2. Schoop (acid)	4.000	11.500	5.750	15.000	11.750	30.500	Only power and sinking fund and interest only on the electrolytic plant.
3. Garuti	5.000	—	7.500	—	15.000	—	Power without general expenses.
4. Schuckert	3.750	9.250	5.500	13.500	11.000	27.250	Without sinking fund and interest on the cost of gasometers, as well as without general expenses.
C. *Total cost of production including sinking fund, interest, and compression of the gases.*							
1. Schmidt	28.750	35.500	38.250	47.000	68.750	86.500	
2. Garuti	5.650	—	8.500	—	14.500	—	Without interest and sinking fund on the investment in flasks as well as general expenses.

electrolytic formation of ferrates may also indeed be assumed to take place, which explanation Haber[1] has fixed upon recently as the result of his extensive study of the subject.

Schmidt says, on the contrary, that after using the apparatus of his system two and a half years, the electrodes had only diminished 1 mm. in thickness. It is, however, to be remembered

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[1] Zeitschr. f. Elektrochemie, 1900–1901.

that Schmidt does not use caustic alkali, but potassium carbonate, which is very free from sulphuric acid and chlorine.

ABSORPTION OF CARBON DIOXIDE.

A further alteration may take place in the charge of the electrolytic apparatus for the decomposition of water, working with caustic alkaline electrolytes, which is due in part to the absorption of carbon dioxide from the atmosphere. On this point it is to be remembered that the most modern apparatus prevent as far as possible the contact of air with the electrolyte, in which a layer of mineral oil upon the surface of the electrolyte gives good service, and that finally with apparatus working at high temperatures a layer of vapor above the electrolyte excludes the carbon dioxide of the atmosphere in a satisfactory manner.

SECURITY FROM EXPLOSIONS.

Concerning the safety of the gases from explosion, the limit of safety with oxygen lies at 90–95 per cent. purity. All of the newer apparatus are completely above the requirements in this respect.

CONCURRENT PROCESSES.

Three groups of processes may be brought out as competitors of the electrolytic decomposition of water, namely:

(1) Other electrochemical processes in which oxygen or hydrogen are obtained as by-products.

(2) Physical processes.

(3) Purely chemical processes.

(1) Electrochemical Processes.

(*a*) Hydrogen.

Hydrogen is the most important of the by-products of electrochemical processes. All those processes which rest upon the electrolytic decomposition of the alkaline chlorides evolve this gas in important amounts. Of these processes, those which work without a separation of the electrode spaces, like the manufacture of chlorates and hypochlorites (usually called electric bleach), hardly permit of the separate utilization of the hydrogen, since, on the one hand, especially with electric bleach, the installation is mostly too small; on the other hand, with both classes of processes, the hydrogen is usually contaminated in not unimportant quantities with the products set free at the anode (O, Cl, etc.). In those processes, on the other hand, which decompose the alkaline chlorides for the purpose of manufacturing separately chlorine and caustic alkali, hydrogen can be obtained in the pure state. In such methods of working, under this heading, which use diaphragms for instance (processes of the Elektron companies), the catching of the hydrogen will entail not very convenient alterations in the apparatus. Such methods have, as a rule, at their best, the cathode spaces only fairly tight. To enclose tightly the cathode spaces would be quite inconvenient when the diaphragms have to be changed. The possibility and the practicability of obtaining hydrogen as a by-product has been already proven. As an example, the Vereinigten Chemischen Fabriken Leopold shall sold compressed hydrogen which had been obtained as a by-product, but its production has since been given up.

The obtaining of hydrogen as a by-product is the easiest with those electrolytic alkali processes which work with mercury cathodes. The amalgam here lies in a space distinct from the decomposing apparatus, and so only this space need be closed air-tight and provided with suitable piping.

This opportunity brings to the author's remembrance a very interesting application of the hydrogen set free by the decomposition of this amalgam. He had at one time the occasion to inspect and report on an experimental plant at Aachen run on the Störmer system. Since the utilization of the hydrogen was not to be thought of on account of the smallness of the plant, Störmer used the same for an empirical control of the efficiency of the apparatus. The hydrogen escaped from the tightly closed amalgam washing apparatus by a narrow vertical tube, was ignited and the height of the flame gave an approximate idea of the efficiency.

Aside from the manufacture of chlorates and electric bleach, omitted for the above explained reasons, we may assume the power used in the various plants which are concerned with the electrolytical decomposition of alkaline chlorides at in round numbers 45,000 kilowatts. If we assume an average current output for all competing processes at 80 per cent., and the average working voltage of 4.5, there results a daily production of hydrogen of 80,000 cubic metres, the greater part of which at present escapes unused.

There is therefore no prospect of success for the electrolytic manufacturer of hydrogen when increasing consumption of the chlorine and alkali plants permits them to bring their by-product, hydrogen, in a compressed state on the market. Those cases are naturally excepted which are so placed with regard to a hydrogen market that the transportation of the compressed product is too high on account of freight.

(*b*) Oxygen.

Other electrochemical processes scarcely enter as competitors for the manufacture of electrolytic oxygen. There is indeed a possibility that oxygen may be produced as a by-product in electrolytic processes working with insoluble anodes. This will, however, in most cases be obtained with hydrogen according to the better or poorer efficiency of the cathodic precipitation.

(2) Physical Processes.

(*a*) Oxygen.

In the line of physical processes, the Linde method of obtaining fluid air is a competitor with which the electrolytic manufacture has to reckon. According to Linde's latest communication[1], he is in a position to produce fluid air with an expenditure of 3 horse-power hours per kilogram with his smaller machines or with his largest type with 2 horse-power hours per kilogram, and believes it possible to reduce the power requirement to 1½ horse-power hour per kilogram.

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[1] Zeitschr. des Vereins deutscher Ing., 1900, 70.

He reckons the total cost of liquid air with large plants at 2½ cents per kilogram. These assumptions do not take into account the large losses which fluid air suffers in transportation.

The possibility of fractioning fluid air into gas mixtures rich in nitrogen and oxygen, respectively, is well known. When the separation takes place at atmospheric pressure the results are as shown in Fig. 85, as given by Linde. At the beginning of the evaporation, the gas mixture consists of about 92 per cent. nitrogen and 8 per cent. oxygen. This relation changes according to the curve *a c b*, on different evaporations. The curve *d e* shows the enriching of the respective values of oxygen. If an electrolytic plant utilizes hydrogen as well as oxygen, it can compete with the Linde process according to the costs of manufacture so far given, assuming similar cost prices for power, because the electrolysis requires a smaller investment in plant and, therefore, a smaller sinking-fund and interest cost. The conditions are not so favorable if the hydrogen cannot be utilized. The figures would be still further to the advantage of Linde if the hopes of this inventor materialize according to which, by utilizing a new principle of construction, he expects to make one cubic metre of gas containing 50 per cent. of oxygen with an expenditure of 1 horse-power hour. In such a case, Linde calculates a total cost of 1 cubic metre of gas containing 50 per cent. of oxygen at 0.625 cent, which is equal to 0.3 cent per horse-power hour.

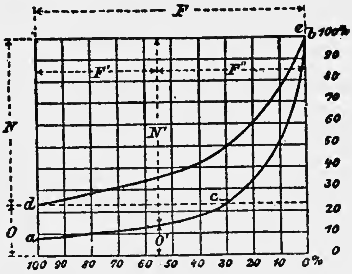

Fig. 85.

The electrolytic oxygen would be able to compete, without doubt, in all those cases in which pure gas must be had, since fluid air under the best conditions furnishes a mixture containing only 70–75 per cent. oxygen. The electrolytic method would, also, according to all probabilities hold the field for small installations.

(3) Chemical.

(*a*) Hydrogen.

The purely chemical methods for obtaining hydrogen includes solution of metals in acids (iron, zinc, etc.). The electrolytic manufacture is technically and economically superior to these processes as will be later shown more in detail.

(*b*) Oxygen.

The chemical process of manufacturing oxygen which rests upon the conversion of the oxygen of the air into chemical compounds which easily give up their oxygen, such as the processes based on barium superoxide, normal plumbates, sodium manganates, etc., furnish only an impure product with about 85 to 90 per cent. oxygen, and what has been said of Linde's fluid air in this respect applies also to them.

The processes for manufacturing oxygen from compounds rich in oxygen such as mercuric oxide, potassium chlorate, manganese dioxide, potassium chromate, etc., are not really at present active competitors of the electrolytic process.

Compression.

Concerning the compression of the gases, it must be remembered that it is not usually carried over 100 to 110 atmospheres and only in extreme cases are pressures of 200 atmospheres used. Schoop gives some details of compression plants in his recently published treatises.[1] The steel flasks are usually made to contain from 10 to 250 litres. The weight is, on the average, 10 kilograms to a cubic metre of gas. The most practicable sizes of flasks are shown in the following table taken from Schoop's work:

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[1] M. U. Schoop: Die industrielle Elektrolyse des Wassers, 1901.

TABLE XI.

Length in metres.	Outer diameter in metres.	Approximate weight in kilograms.	Water in litres.	Price of the empty flasks in dollars.
0.432	0.076	6	1.40	6.00
0.609	0.102	11	3.68	6.75
0.600	0.140	20	7.00	7.50
0.930	0.140	20	11.00	8.25
1.346	0.140	40	16.70	11.75
1.090	0.203	45	26.80	15.00
2.000	0.205	73	50.00	20.00

Some producers of oxygen and hydrogen in order to render certain the recognition of the oxygen and hydrogen flasks from each other, provide the oxygen flasks with right-handed valves and the hydrogen flasks with left-handed valves and black nozzles.

Special Applications.

The uses of oxygen and hydrogen and the mixed gases are generally known and will here be collected as a conclusion of this Monograph, and some new propositions concerning their use alluded to more at length.

(1) Detonating Gas.

(*a*) HIGH TEMPERATURE.

For high temperatures, in particular the working of metals: This application dates back to the work of St. Claire-Deville who melted platinum in the oxyhydrogen flame. In many cases the electric furnace can be replaced by the oxyhydrogen flame and in this connection we may recall the attempts to manufacture calcium carbide without the electric current. More recently the question of using mixed gas in glass furnaces has regained interest. An investigation of Ascherl has been in this direction. The manufacture of large glass vessels from plates of glass, melting down the joints with the oxyhydrogen flame, is carried out in England on an industrial scale.

The oxyhydrogen flame has gained an important place in many cases in the working of metals where the nature of the metal is such as to exclude the use of carbonaceous gas even when mixed with oxygen. A content of carbon either hinders in most cases the soldering entirely, or deteriorates the quality of the metal soldered. Repairing of water-tube boilers can be easily accomplished with an oxyhydrogen flame.

We shall speak of the soldering of lead further on when treating of the applications of hydrogen, since mixed gas is not used for this purpose but a mixture of hydrogen and oxygen poorer in the latter.

(*b*) LIGHTING.

Lighting: Mixed gas has been used for this purpose for a long time for the so-called Drummond lime light, and has attained, for special purposes, a certain sphere of usefulness, although a limited one. In the recent Spanish-American war it was used on a large scale for search-lights.

Mixed gas never was able to hold a place for general lighting purposes in spite of the stirring activity which many investigators have shown in this direction. The principal difficulty is indeed in the great danger of explosion, and the difficulty of obtaining durable incandescent material. Investigation in this direction has not yet been given up. For instance, there lies before the author a recently allowed Austrian patent of the 15th of May, 1901, to Urbanitzky.

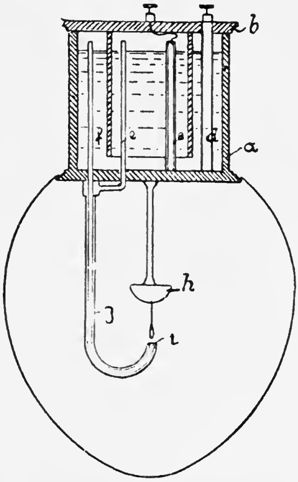

Fig. 86.

According to this, the electrolysis of the water takes place at each lamp and the mixed gas makes an incandescent substance glow. In the drawing, shown in Fig. 86, *a b* is the decomposition vessel, *c d* the electrodes, *e f* the gas-exit tubes which end in the double tube *g*, *h* the glowing body, and *i* the igniting device for the mixed gas.

Quite aside from the conditions and considerations of technical operation, the patentee seems to have quite forgotten what sized section of conductors he would require to conduct to each single lamp the necessary current for the decomposition of water at the low tension of 2.5 to 3 volts.

(*c*) BLASTING PURPOSES.

Blasting purposes. The attempts to use mixed gas for blasting purposes are not so generally known.

Siemens & Halske, A. G., in Vienna, took up experiments in 1893 to apply electrolysis directly to blasting purposes. The first experiment was to produce haloid nitrogen compounds in small, thick capsules at the place where it was to be ignited. Later the investigations were extended to compressed oxyhydrogen gas. The decomposing apparatus were thick-walled, pear-shaped, glass flasks with two platinum wires sealed therein (Fig. 87).

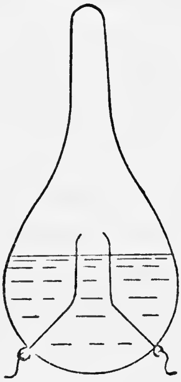

Fig. 87.

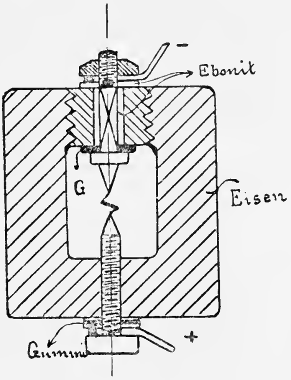

Fig. 88.

These were filled with the electrolyte so far that the platinum wires were not entirely submerged and then sealed. The ignition was produced after the electrolysis had been finished by connecting the poles with an induction coil. Larger experiments were made with the apparatus shown in Fig. 88. The affair was not further investigated because, primarily, of difficulties with the patent.

Ochse tried to utilize the same idea.[1] He used steel cylinders, 180 mm. long, closed by a stopper which carries the electrodes and the igniting apparatus. These cylinders can withstand a pressure of 1200 atmospheres and contain 22.5 grams of water and 2.5 grams of soda solution. Using 8 to 10 volts tension, a current strength of 0.8 to 1 ampere was obtained. The electrolysis was continued until 20 grams of water were decomposed and then the explosion of the mixed gas produced by an induction spark. The explosive power of such a cartridge is stated to be equivalent to 150 grams of modern safety explosive containing ammonium nitrate (roburite, bellite, securite, etc.). Cornara has embodied the same idea in the English patent, 302,53 of the 21st of December, 1897, except that the shape of the cartridge was somewhat modified.

More recently it appears that investigators have given up the idea of generating and compressing the mixed gas in the cartridge itself. The attempts to use mixed gas for blasting purposes have taken more the direction of manufacturing the mixture of gases outside the cylinder and then compressing it mechanically into the latter.

As an example of such a cartridge, we illustrate in Fig. 89 the Boehm filling arrangement for oxyhydrogen-blasting cartridges patented in Germany 107,531.

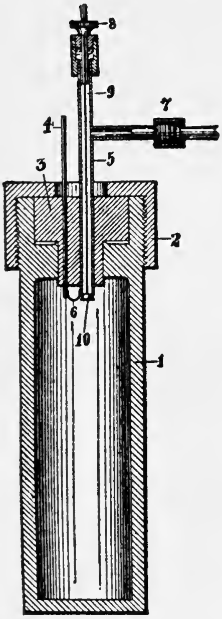

Fig. 89.

In this:

1. The cartridge case.
2. The screwed in closing head.
3. The joint stopper.
4. The igniting electrode.
5. The steel tube for filling the cartridge and likewise acting as the second electrode.
6. The igniting filament.
7. The screw attachment for fastening to the air-pump.
8. The screw for adjusting the valve stem.
9. The valve stem.
10. The cone joint.

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[1] D. R. P., 67153. Jacobsen, Repertorium 1893., I, 238. El. Engineer, London, XXVII, No. 19, 13 May, 1898. Electrochem. Ztschr., 1898–99., 127.

We cannot so far speak of the definite introduction of oxyhydrogen blasting, either by the direct or indirect production of the gases.

(2) Hydrogen.

(*a*) BALLOONING PURPOSES.

Ballooning: For this purpose hydrogen has been used for a long time, and the electrolytic production of hydrogen has by far surpassed all other methods of producing it. For the purposes of ballooning, the hydrogen should be as pure as possible in order that the lifting power of the balloon may be the greatest possible with the smallest possible cubical content. By doing so, on the one hand, expensive balloon material is spared; on the other hand, the cost of transportation of the compressed gas is less. It may be observed that hydrogen obtained in the chemical way from iron and sulphuric acid is nearly double as heavy as the pure gas (160 : 89), while electrolytic hydrogen can be obtained easily only about 25 per cent. heavier than the pure gas.[1] Up to the present, the Italian, French and Swiss army bureaus manufacture their hydrogen for balloon purposes electrolytically. The German army uses compressed by-product hydrogen from the electrolytic alkaline chloride plants.

(*b*) SOLDERING PURPOSES.

Soldering purposes: In this line the most prominent applications are in the manufacture of accumulators, and in the sulphuric acid works for the purpose of soldering lead.

Clean lead surfaces, it is well known, may be easily soldered with a blowpipe with a hydrogen-air flame. The hydrogen necessary for this was formerly exclusively manufactured by the use of crude zinc and dilute sulphuric acid (15 and 20 per cent.). It would lead us here too far to discuss the more usual chemical apparatus employed for evolving this hydrogen and so we refer as far as concerns it to the literature of this subject.[2]

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[1] W. Dürer: Electrochemische Zeitschr., **VIII**, 2 (1901).

[2] Z. B. P. Schoop: Die Sekundärelemente, **II**, 41 (1895). Zeitschr. f. Elektrochemie, **II**, 203 (1895–96).

One of the principal disadvantages of the chemical process lies in the circumstance that in dissolving the zinc in sulphuric acid the arsenic in the latter is evolved as hydrogen arsenide according to the equation

$$As_2O_3 + 6H_2SO_4 + 6Zn = 2AsH_3 + 3H_2O + 6ZnSO_4.$$

A content of 0.5 per cent. of arsenic is not unfrequently found in sulphuric acid and it is, therefore, easily seen that constant working under such conditions with hydrogen generators, which are often not perfectly tight and thereby allow unburned gas to escape from burners which are extinguished but not entirely turned off, results in the most disagreeable sanitary consequences for the workmen. For this reason the accumulator constructors themselves have proposed to pass this chemically prepared hydrogen through red hot copper tubes and afterwards to cool it, by which operation the arsenic is seperated out, or the gas is freed from arsenic by washing with potassium permanganate solution.[1]

These sanitary difficulties are naturally completely avoided by the use of electrolytic hydrogen. Also the danger of explosion in the apparatus itself is less with this manner of manufacture. Finally when using electrolytic hydrogen generators, the oxygen simultaneously generated can be used in place of air in the blast-flame, which results in a saving of about 50 per cent. of the time necessary for soldering.

Also from the point of view of economy the electrolytic method of manufacture has the advantage over the chemical.

For 1 kilogram of zinc costing, to-day, 8¾ cents, 2 kilograms of sulphuric acid are required, costing 3½ cents. For this outlay of 12¼ cents there is theoretically only 32 grams or not quite 360 litres of hydrogen to be obtained. Since the zinc and acid are not completely used up, it may be assumed that 800 ampere-hours would electrolytically produce an equal volume of hydrogen. Using 2.5 volts working tension, 2 kilowatt hours would be necessary, which, at the price of

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[1] P. Schoop: Die Sekundärelemente, II, 45, (1895).

power already assumed—¼ to 1¼ cents, would cost ½ to 2½ cents.

The total costs for the soldering have been determined by the results of operation in various accumulator factories to be about one-half cheaper with the electrolytic apparatus than with the chemically generated hydrogen. Besides the economy in the cost of gas and time, there can also be taken into consideration the diminution of the labor required.

The gas must naturally be compressed for use outside, yet the weights to be transported in gas flasks are no greater in the one case than in the other.

M. U. Schoop has recently published an interesting dissertation on the soldering of lead with compressed oxygen and hydrogen.[1] Since this, however, does not include the electrolytic production of the gases, but only their use after being compressed and their extensive applications in this direction, we refer to the original paper.

It may be, however, mentioned that since the soldering flame must have reducing qualities, when electrolytically produced gas is used, there is a certain excess of unused oxygen. The gases are consumed in the proportion of 1 hydrogen to ⅓ oxygen instead of 1 hydrogen to ½ oxygen as furnished by the electrolyzers.

Soldering with the soldering iron and easily fusible solder often competes with the hydrogen soldering, yet according to the reports of professional people a cleaner lead surface is necessary and the quality of the soldered joint is not equal to that produced by the autogenous soldering of the lead, quite aside from the considerations of the sanitary inconveniences resulting from the content of mercury in the easily fusible solder.

In the sulphuric acid industry the hydrogen soldering with electrolytically generated gas is of particular importance because of the quick soldering of vertical seams.

Heraeus in Hanau has used with good success the blast-flame with a large excess of hydrogen for the autogenous

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[1] Zeitschr. f. Elektrotechnik, Wien, XIX 224, (1901).

soldering of aluminium. The samples of work shown at the Paris Exposition attracted considerable attention.

(*c*) LIGHTING.

Lighting: The attempts for using hydrogen for the purposes of lighting go back to the year 1846 when Gillard, in France, introduced a process by which a little basket of platinum wire was brought to a white heat by burning hydrogen. A successful result was not obtained, as was also the result of attempts of White and Leprince to use carburized hydrogen. More recently Schmidt has taken up the application of hydrogen for lighting purposes in combination with the Auer (Welsbach) mantle.

Schmidt first presented his views upon this subject before the Seventh Yearly Assembly of the German Electrochemical Society in Zurich, in 1900, and a lively debate arose on the subject, in which especially Nernst brought out the high requirements of the mantles for the use of hydrogen gas, and Förster the difficult question of suitable stop-cocks.

Concerning the views of Schmidt he has most accurately expressed them to the author in a long private communication, the most important of them being here reproduced in abstract:

The most advantageous qualities of hydrogen which appear to make it well suited for lighting purposes are its harmlessness for the human organs and high heat of combustion, the small weight, the relatively high ignition point, the easy conductibility, and the chemical inactivity of the same towards the fittings. Its combustion produces only water vapor, no foul smelling products, and it takes from the atmosphere the smallest amount of oxygen. The flame is really non-luminous but will heat a Welsbach mantle to the brightest, white heat, whereby a mantle of ordinary size will give a far too great amount of light (several hundred candle-power) for ordinary purposes.

Schmidt uses, therefore, in his light investigations, a very much smaller mantle, about 6 cm. long and 0.5 cm. in diameter, one of which is shown in Fig. 90. The smaller dimensions makes the mantle more proof against damage by vibrations.

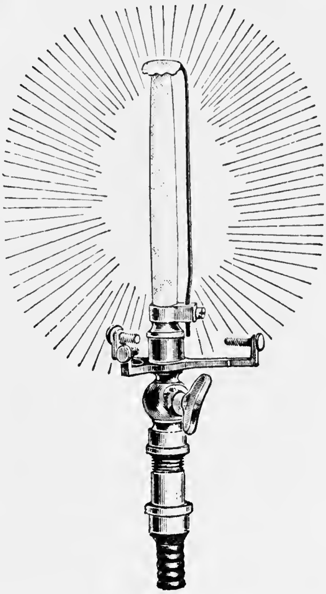

Fig. 90.—Burner for hydrogen light.

The difficulties named by Nernst of the greater requirements of a mantle for withstanding the hydrogen flame are, according to the view of Schmidt, balanced by the circumstances that the hydrogen contains no impurities, as iron compounds and dust which in other cases affect the durability of the mantles. The inconvenient quality of being without odor is shared by both hydrogen and water-gas, and this difficulty in the use of the gas for lighting can be overcome in the case of hydrogen in the same way it is managed with water, *i. e.*, by introducing into it small quantitities of mercaptan vapor.

A very small amount of hydrogen gas needs to be used on account of its high temperature of combustion.

Schmidt compares in his experiments hydrogen with illuminating gas and acetylene, and believes the superiority of the first to be proven by the following facts:

(1) Sanitary advantage, since only water vapor results as a product of combustion and the minimum amount of oxygen is withdrawn from the atmosphere with a much less development of heat.

(2) A very much smaller section of piping required. These are for hydrogen, used at a similar pressure and volume, one-eighth the size necessary for illuminating gas and one-tenth that for acetylene. Referred to the candle-power developed, the sizes of piping necessary for hydrogen is only one-fifteenth and one-ninth that needed for the other gases.

(3). Very much easier and less dangerous compressibility to many hundred atmospheres without altering the qualities of the gas, while illuminating gas is rendered valueless by compression, the oil and fat gas used for lighting cars can be compressed only to 10 atmospheres and acetylene cannot be compressed higher than 2 atmospheres on account of the danger of explosions.

(4). The possibility of higher pressures in the gas pipes, so that the flame may be turned in any direction, even downwards, which is practicable with a pressure of 200 mm. of water.

(5). Smaller dangers of explosions since the latter can only take place when it contains 9.5 per cent. of air, on the contrary with acetylene when it contains 3.8 per cent., with illuminating gas 8 per cent.; since the diffusibility of hydrogen is twenty times greater than that of air the mixing of the gas with the air takes place much more rapidly.

Concerning the cost of lighting with hydrogen, Schmidt gives the following comparative figures for the above mentioned kinds of gas.

Using illuminating gas with a heat value of 5000 calories when burned in a Welsbach burner, there is used per normal candle-power hour 2.1 litres, if used at 220 mm. pressure 1 litre, with hydrogen somewhat less than 1 litre, with acetylene 0.75 litre, and with the proposed but not yet achieved combustion of the latter in the Welsbach mantle 0.36 litre.

Since the consumption of gas varies naturally with the strength of the flame, Schmidt found the consumption of hydrogen per candle-power hour to be in small burners 1.5 litres for each burner, for large burners 1 litre, and as an average 1.25 litres.

With reference to their production by means of electricity, the present values between the hydrogen light and the calcium carbide, that is, acetylene, is to the advantage of the former. One kilowatt day produces 4 cubic metres of hydrogen and equals 3200 candle-power hours on the one hand, and 4 kilograms of calcium carbide equivalent to 1200 litres of acetylene or 1600 candle-power hours on the other. In this presentation, however, the very much greater consumption of raw materials and electrodes in the production of calcium carbide in comparison with the electrolysis of water has not been taken into account. In order to attain a more exact basis of comparison, Schmidt starts with the market price of calcium carbide and calculates the same as 6¼ cents per kilogram, the cost production being 3.625 cents. Out of the latter figures, 1.25 cents is referable to raw materials and its preparation so that 2.375 cents remains for current, furnacing, and general expenses. If the current is reckoned at one cent, there remains for the power only 0.165 cent kilowatt hour, a price only possible in very large plants.

Assuming a cost price of 3.625 cents per kilogram of carbide from which 400-candle-power is obtainable, there could be obtained electrolytic hydrogen to a volume of 1540 litres or 1230 candle-power hours.

As against this better utilization of power in the manufacture of hydrogen must, however, be placed the easier storage and carriage of calcium carbide. Schmidt makes the following comparisons with reference to the consumption of power for the compression of hydrogen, freight costs for transportation and return of the flasks (10 kilograms per cubic metre), and sinking fund on the assumption of twenty shipments per year.

The cost of 10,000 candle-power hours transported 500 kilometres (300 miles):

From carbide.	
26 kg. of carbide	$ .90
Packing	.10
Evolution of acetylene, purification and interest on apparatus	.10
Freight 300 miles	.125
	$1.225

From hydrogen.	
12.5 cubic metres of hydrogen	$ .295
Compression	.025
Interest on flasks	.1625
Emptying and adjusting valves	.0200
Freight and return for 300 miles	.6250
	$1.1275

It is seen from this comparison that the distance of 300 miles is about the limit at which hydrogen can compete with acetylene.

For small distances, distribution in pipes would naturally be used. What difficulties would in that case be encountered in preserving the tubes gas-tight cannot be necessarily foretold from an experimental study of the subject.

(*d*) MOTOR PURPOSES.

Motor purposes: The evident applicability of hydrogen for motor purposes has likewise been often taken into consideration, but at the present no results worth mentioning have been obtained.

(3) Oxygen.

Concerning, finally, the application of oxygen there is no question that with a sufficiently low price, quite a number of extended applications would be found. The hastening of oxidation processes and intensifying of combustion is in many cases the end which is being actively sought after. In many steel works, electrolytic oxygen is at present being experimentally used in place of air in the Bessemer converter. Even in various blast-furnace processes the application of oxygen has been thought of if the difficulties could be overcome in finding a suitable material for constructing the furnace.

Investigations in the glass industry have shown that the introduction of oxygen into the fluid mass of glass results in an economy of 40 to 50 per cent. in labor, time, fuel and deterioration, without damaging the quality of the glass. The extensive application of oxygen in the manufacture of sulphuric acid according to the contact process is indeed only a question of time.

In organic technology, oxygen is already used for many purposes. It is used, for instance, partly as ozone for the ageing of alcoholic beverage, in the manufacture of varnishes, and in the purification of illuminating gas. More recently oxygen has been used in the preservation of milk, the freshly obtained milk being saturated with oxygen at a pressure of 5 to 6 atmospheres and allowed to stand several hours under this pressure. After diminishing the pressure to two atmospheres, the milk is ready for transportation.

In the production of ozone, oxygen would be used in all those cases in place of air, in which the introduction of nitrogen compounds into the product treated with ozone is to be avoided.

Finally compressed oxygen has manifold uses in medicine and hygiene, and in particular for the improvement of the air in rooms where renewal of the air is not possible, also for instance in mines and at fires or under such conditions where very attenuated air makes breathing difficult, as in balloon ascensions.

It would surpass the limits of this volume to go into the methods of analysis of the gases of which we have treated, and concerning this subject we refer to the numerous special treatises.[1]

There remains only to the author the agreeable duty to thank most heartily Messrs. Dr. Hammerschmidt, of Nürnberg, Dr. Schmidt, of Zurich, and M. U. Schoop, of Cologne, for the furnishing of original material, and also Dr. Abel, of Vienna, for friendly help in the reading of the proof.

[1] Bunsen: Gasometrische Methoden. W. Hempel: Gasanalytische Methoden, II Auflage, 1890. Cl. Winkler: Lehrbuch der technischen Gasanalyse, III Auflage, 1901: B. Neumann: Gasanalyse und Gasvolumetrie, 1901.

TABLE XII.

REDUCTION OF GAS VOLUME TO A BAROMETRIC PRESSURE OF 760 MM.

(Taken from Lunge, Chem.-tech. Untersuchungsmethoden, I [1899] Appendix, pages 12-17). The Pressure Read Off on the Barometer is to be Diminished from Temperatures between 0° and 12° about 1 mm., for 13°-19° about 2 mm., and for 20°-25° about 3 mm.

760	730	732	734	736	738	740	742	744	746	748	750	752	754	756	758	762	764	766	768	770	760
1	0.961	0.963	0.966	0.968	0.971	0.974	0.976	0.979	0.982	0.984	0.987	0.989	0.992	0.995	0.997	1.003	1.005	1.008	1.011	1.013	1
2	1.921	1.926	1.932	1.937	1.942	1.947	1.953	1.958	1.963	1.968	1.974	1.979	1.984	1.989	1.995	2.005	2.011	2.016	2.021	2.026	2
3	2.882	2.889	2.898	2.905	2.913	2.921	2.929	2.937	2.945	2.953	2.960	2.968	2.976	2.984	2.992	3.007	3.016	3.024	3.032	3.039	3
4	3.842	3.852	3.864	3.874	3.884	3.895	3.905	3.916	3.926	3.937	3.947	3.958	3.968	3.979	3.990	4.010	4.021	4.032	4.042	4.052	4
5	4.803	4.816	4.830	4.842	4.855	4.868	4.882	4.895	4.908	4.921	4.934	4.947	4.960	4.974	4.987	5.013	5.026	5.040	5.053	5.066	5
6	5.763	5.779	5.796	5.810	5.826	5.842	5.858	5.874	5.890	5.905	5.921	5.937	5.952	5.968	5.984	6.016	6.032	6.047	6.063	6.079	6
7	6.724	6.742	6.762	6.779	6.797	6.816	6.834	6 853	6.871	6.889	6.908	6.926	6.944	6.963	6.982	7.018	7.037	7.055	7.074	7.092	7
8	7.684	7.705	7.728	7.747	7.768	7.790	7.810	7.832	7.853	7.874	7.894	7.916	7.936	7.958	7.979	8.021	8.042	8.063	8.084	8.106	8
9	8.645	8.668	8.693	8.716	8.739	8.763	8.787	8.811	3.834	8.858	8.881	8.905	8.929	8.952	8.977	9.023	9.048	9.071	0.095	9.119	9
10	9.61	9.63	9 66	9.68	9.71	9 74	9.76	9.79	9.82	9.84	9.87	9.89	9.92	9.95	9.97	10.03	10.05	10.08	10.11	10.13	10
20	19 21	19.26	19.32	19.37	19.42	19.47	19.53	19.58	19.63	19.68	19.74	19.79	19.84	19.89	19.95	20.05	20.11	20.16	20.21	20.26	20
30	28.82	28.89	28.97	29.05	29.13	29.21	29.29	29.37	29.45	29.53	29.60	29.68	29.76	26.84	29.92	30.07	30.16	30.24	30.32	30.39	30
40	38 42	38.52	38.64	38.74	38.84	38.95	39.05	39.16	39.26	39.37	39.47	39.58	39 68	39.79	39.90	40 01	40.21	40.32	40.42	40.52	40
50	48.03	48.16	48.30	48.42	48.55	48.68	48.82	48.95	49.08	49.21	49.34	49.47	49.60	49.74	49.87	50.13	50.26	50.40	50.53	50.66	50
60	57.63	57.79	57.95	58.10	58 26	58.42	58.58	58.74	58.90	59.05	59.21	59.37	59.52	50.68	59.84	60.16	60.32	60 47	60.63	60.79	60
70	67.24	67.42	67.61	67.79	67.97	68.16	68.34	68.53	68.71	68.89	69.08	69.26	69.44	69.63	69.82	70.18	70.37	70.55	70.75	70.92	70
80	76.84	77.05	77.27	77.47	77.68	77.90	78.10	78.32	78.53	78.74	78.94	79.16	79.36	79.58	79.79	80.21	80.42	80.63	80.84	81.06	80
90	86.45	86.68	86.93	87.16	87.39	87.63	87.87	88.11	88.34	88.58	88.81	89 05	89.29	89.52	89.77	90.23	90.48	90.71	90.95	91.19	90
100	96.05	96.32	96.58	96.84	97.11	97.37	97.36	97.89	98.16	98.42	98.68	68.95	99.21	99.47	99.74	100.26	100.53	100.79	101.05	101.32	100

TABLE XIII.

Reduction of Gas Volume to Temperature of 0° C.

(Lunge, Chem.-tech. Untersuchungsmethoden I [1899] Appendix, pages 6–11.)

cc. at 0°.	1°	2°	3°	4°	5°	6°	7°	8°	9°	10°	11°	12°	13°	14°	15°	cc. at 0°.
1	0.996	0.993	0.989	0.986	0.982	0.978	0.975	0.972	0.968	0.965	0.961	0.958	0.955	0.951	0.948	1
2	1.993	1.985	1.978	1.971	1.964	1.957	1.950	1.943	1.936	1.929	1.923	1.916	1.909	1.903	1.986	2
3	2.989	2.978	2.967	2.957	2.946	2.936	2.925	2.915	2.904	2.894	2.884	2.874	2.864	2.854	2.844	3
4	3.985	3.971	3.956	3.942	3.928	3.914	3.900	3.886	3.872	3.859	3.845	3.832	3.818	3.805	3.792	4
5	4.982	4.964	4.946	4.928	4.910	4.893	4.875	4.858	4.841	4.824	4.807	4.790	4.773	4.757	4.740	5
6	5.978	5.956	5.935	5.913	5.892	5.871	5.850	5.830	5.809	5.788	5.768	5.747	5.728	5.708	5.688	6
7	6.974	6.949	6.924	6.899	6.874	6.850	6.825	6.801	6.777	6.753	6.729	6.705	6.682	6.659	6.636	7
8	7.970	7.942	7.913	7.885	7.856	7.828	7.800	7.773	7.745	7.718	7.690	7.663	7.637	7.610	7.584	8
9	8.967	8.934	8.902	8.870	8.838	8.807	8.775	8.744	8.713	8.682	8.652	8.621	8.591	8.562	8.532	9
10	9.963	9.927	9.891	9.856	9.820	9.785	9.750	9.716	9.681	9.647	9.613	9.579	9.546	9.513	9.480	10
20	19.93	19.85	19.78	19.71	19.64	19.57	19.50	19.43	19.36	19.29	19.23	19.16	19.09	19.03	18.96	20
30	29.89	29.78	29.67	29.57	29.46	29.36	29.25	29.15	29.04	28.94	28.84	28.74	28.64	28.54	28.44	30
40	39.85	39.71	39.56	39.42	39.28	39.14	39.00	38.86	38.72	38.59	38.45	38.32	38.18	38.05	37.92	40
50	49.82	49.64	49.46	49.28	49.10	48.93	48.75	48.58	48.41	48.24	48.07	47.90	47.73	47.57	47.40	50
60	59.78	56.56	59.35	59.13	58.92	58.71	58.50	58.30	58.09	57.88	57.68	57.47	57.28	57.08	56.88	60
70	69.74	69.49	69.24	68.99	68.74	68.50	68.25	68.01	67.77	67.53	67.29	67.05	66.82	66.59	66.36	70
80	79.70	79.42	79.13	78.85	78.56	78.28	78.00	77.73	77.45	77.18	76.90	76.63	76.37	76.10	75.84	80
90	89.67	89.34	89.02	88.70	88.38	88.07	87.75	87.44	87.13	86.82	86.52	86.21	85.92	85.62	85.32	90
100	99.63	99.27	98.91	98.56	98.20	97.85	97.50	97.16	96.81	96.47	96.13	95.79	95.46	95.13	94.80	100

TABLE XIII.—(*Continued.*)

cc. at 0°.	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°	26°	27°	28°	29°	cc. at 0°.
1	0.945	0.941	0.938	0.935	0.932	0.929	0.926	0.922	0.919	0.916	0.913	0.910	0.907	0.904	1
2	1.889	1.883	1.876	1.869	1.864	1.857	1.851	1.845	1.839	1.832	1.826	1.820	1.814	1.808	2
3	2.834	2.824	2.815	2.805	2.795	2.786	2.777	2.767	2.758	2.749	2.739	2.730	2.721	2.712	3
4	3.779	3.766	3.753	3.740	3.727	3.714	3.702	3.690	3.677	3.665	3.652	3.640	3.628	3.616	4
5	4.724	4.707	4.691	4.675	4.659	4.643	4.628	4.612	4.597	4.581	4.566	4.551	4.535	4.520	5
6	5.668	5.648	5.629	5.609	5.591	5.572	5.553	5.534	5.516	5.497	5.479	5.461	5.442	5.424	6
7	6.613	6.590	6.567	6.544	6.523	6.500	6.479	6.457	6.435	6.413	6.392	6.371	6.349	6.328	7
8	7.558	7.531	7.506	7.479	7.454	7.429	7.404	7.379	7.354	7.330	7.305	7.281	7.256	7.232	8
9	8.502	8.472	8.444	8.414	8.386	8.357	8.330	8.302	8.274	8.246	8.218	8.191	8.163	8.136	9
10	9.447	9.414	9.382	9.349	9.318	9.286	9.225	9.224	9.193	9.162	9.131	9.101	9.070	9.040	10
20	18.89	18.83	18.76	18.69	18.64	18.57	18.51	18.45	18.39	18.32	18.26	18.20	18.14	18.08	20
30	28.34	28.24	28.15	28.05	27.95	27.86	27.27	27.77	27.58	27.49	27.39	27.30	27.21	27.12	30
40	37.79	37.66	37.53	37.40	37.27	37.14	37.02	36.90	36.77	36.65	36.52	36.40	36.28	36.16	40
50	47.24	47.07	46.91	46.75	46.59	46.43	46.28	46.12	45.97	45.81	45.66	45.51	45.35	45.20	50
60	56.18	56.48	56.29	56.09	55.91	55.72	55.53	55.34	55.16	54.97	54.79	54.61	54.42	54.24	60
70	66.13	65.90	65.67	65.44	65.23	65.00	64.79	64.57	64.35	64.13	63.92	63.71	63.49	63.28	70
80	75.58	75.31	75.06	74.79	74.54	74.29	74.04	73.79	73.54	73.30	73.05	72.81	72.56	72.32	80
90	85.02	84.72	84.44	84.14	83.86	83.57	83.30	83.02	82.74	82.46	82.18	81.91	81.63	81.36	90
100	94.47	94.14	93.82	93.49	93.18	92.86	92.55	92.24	91.93	91.62	91.31	91.01	90.70	90.40	100

TABLE XIV.

TENSION OF WATER VAPOR IN MM. OF MERCURY FOR TEMPERATURES BETWEEN —2° C. to +35° C.

(From Regnault's Messungen berechnet von Broch, see Trav. et Mém. du Bur. intern. des Poids et Mes. I. A. page 33, 1881.)

°C.	Tension. mm.	°C.	Tension. mm.	°C.	Tension. mm.	°C.	Tension. mm.	°C.	Tension. mm.
—2.0	3.950	+1.7	5.161	+5.3	6.643	+ 9.0	8.548	+12.7	10.921
1.9	3.979	1.8	5.198	5.4	6.689	9.1	8.606	12.8	10.993
1.8	4.008	+1.9	5.235	5.5	6.736	9.2	8.664	+12.9	11.065
1.7	4.038			5.6	6.782	9.3	8.722		
1.6	4.067	+2.0	5.272	5.7	6.829	9.4	8.781	+13.0	11.137
1.5	4.097	2.1	5.309	5.8	6.876	9.5	8.840	13.1	11.210
1.4	4.127	2.2	5.347	+5.9	6.924	9.6	8.899	13.2	11.283
1.3	4.157	2.3	5.385			9.7	8.959	13.3	11.356
1.2	4.188	2.4	5.424	+6.0	6.971	9.8	9.019	13.4	11.430
—1.1	4.218	2.5	5.462	6.1	7.020	+ 9.9	9.079	13.5	11.505
		2.6	5.501	6.2	7.068			13.6	11.580
—1.0	4.249	2.7	5.540	6.3	7.117	+10.0	9.140	13.7	11.655
0.9	4.280	2.8	5.579	6.4	7.166	10.1	9.201	13.8	11.731
0.8	4.312	+2.9	5.618	6.5	7.215	10.2	9.262	+13.9	11.807
0.7	4.343			6.6	7.265	10.3	9.324		
0.6	4.375	+3.0	5.658	6.7	7.314	10.4	9.386	+14.0	11.884
0.5	4.406	3.1	5.698	6.8	7.365	10.5	9.449	14.1	11.960
0.4	4.438	3.2	5.738	+6.9	7.415	10.6	9.512	14.2	12.038
0.3	4.471	3.3	5.779			10.7	9.575	14.3	12.116
0.2	4.503	3.4	5.820	+7.0	7.466	10.8	9.639	14.4	12.194
—0.1	4.536	3.5	5.860	7.1	7.517	+10.9	9.703	14.5	12.273
		3.6	5.902	7.2	7.568			14.6	12.352
0.0	4.569	3.7	5.943	7.3	7.620	+11.0	9.767	14.7	12.432
+0.1	4.602	3.8	5.985	7.4	7.672	11.1	9.832	14.8	12.512
0.2	4.635	+3.9	6.027	7.5	7.725	11.2	9.897	+14.9	12.593
0.3	4.668			7.6	7.777	11.3	9.962		
0.4	4.702	+4.0	6.069	7.7	7.830	11.4	10.028	+15.0	12.674
0.5	4.736	4.1	6.112	7.8	7.883	11.5	10.095	15.1	12.755
0.6	4.770	4.2	6.155	+7.9	7.937	11.6	10.161	15.2	12.837
0.7	4.805	4.3	6.198			11.7	10.228	15.3	12.920
0.8	4.839	4.4	6.241	+8.0	7.991	11.8	10.296	15.4	13.003
+0.9	4.874	4.5	6.285	8.1	8.045	+11.9	10.364	15.5	13.086
		4.6	6.328	8.2	8.100			15.6	13.170
+1.0	4.909	4.7	6.373	8.3	8.155	+12.0	10.432	15.7	13.254
1.1	4.944	4.8	6.417	8.4	8.210	12.1	10.501	15.8	13.339
1.2	4.980	+4.9	6.462	8.5	8.266	12.2	10.570	+15.9	13.424
1.3	5.016			8.6	8.321	12.3	10.639		
1.4	5.052	+5.0	6.507	8.7	8.378	12.4	10.709	+16.0	13.510
1.5	5.088	5.1	6.552	8.8	8.434	12.5	10.780	16.1	13.596
+1.6	5.124	+5.2	6.597	+8.9	8.491	+12.6	10.850	+16.2	13.683

TABLE XIV.—(*Continued.*)

°C.	Tension. mm.	°C.	Tension. mm.	°C.	Tension. mm.	°C.	Tension. mm.	°C.	Tension. n
+16.3	13.770	+20.1	17.471	+23.8	21.888	+27.5	27.258	+31.2	33.749
16.4	13.858	20.2	17.579	+23.9	22.020	27.6	27.418	31.3	33.942
16.5	13.946	20.3	17.688			27.7	27.578	31.4	34.136
16.6	14.035	20.4	17.797	+24.0	22.152	27.8	27.740	31.5	34.330
16.7	14.124	20.5	17.907	24.1	22.286	+27.9	27.902	31.6	34.526
16.8	14.214	20.6	18.018	24.2	22.420			31.7	34.722
+16.9	14.304	20.7	18.129	24.3	22.554			31.8	34.920
		20.8	18.241	24.4	22.690	+28.0	28.065	+31.9	35.119
+17.0	14.395	+20.9	18.353	24.5	22.826	28.1	28.229		
17.1	14.486			24.6	22.963	28.2	28.394		
17.2	14.578			24.7	23.100	28.3	28.560	+32.0	35.318
17.3	14.670	+21.0	18.466	24.8	23.239	28.4	28.726	32.1	35.519
17.4	14.763	21.1	18.580	+24.9	23.378	28.5	28.894	32.2	35.720
17.5	14.856	21.2	18.694			28.6	29.062	32.3	35.923
17.6	14.950	21.3	18.808			28.7	29.231	32.4	36.126
17.7	15.044	21.4	18.924	+25.0	23.517	28.8	29.401	32.5	36.331
17.8	15.136	21.5	19.040	25.1	23.658	+28.9	29.572	32.6	36.536
+17.9	15.234	21.6	19.157	25.2	23.799			32.7	36.743
		21.7	19.274	25.3	23.941	+29.0	29.744	32.8	36.950
+18.0	15.330	21.8	19.392	25.4	24.084	29.1	29.916	+32.9	37.159
18.1	15.427	+21.9	19.510	25.5	24.227	29.2	30.090		
18.2	15.524			25.6	24.371	29.3	30.264	+33.0	37.369
18.3	15.621	+22.0	19.630	25.7	24.516	29.4	30.440	33.1	37.580
18.4	15.719	22.1	19.750	25.8	24.662	29.5	30.616	33.2	37.791
18.5	15.818	22.2	19.870	+25.9	24.808	29.6	30.793	33.3	38.004
18.6	15.917	22.3	19.991			29.7	30.971	33.4	38.218
18.7	16.017	22.4	20.113	+26.0	24.956	29.8	31.149	33.5	38.433
18.8	16.117	22.5	20.236	26.1	25.104	+29.9	31.329	33.6	38.649
+18.9	16.218	22.6	20.359	26.2	25.252			33.7	38.866
		22.7	20.482	26.3	25.402	+30.0	31.510	33.8	39.084
+19.0	16.319	22.8	20.607	26.4	25.552	30.1	31.691	+33.9	39.303
19.1	16.421	+22.9	20.732	26.5	25.703	30.2	31.873		
19.2	16.523			26.6	25.855	30.3	32.057	+34.0	39.523
19.3	16.626			26.7	26.008	30.4	32.241	34.1	39.744
19.4	16.730	+23.0	20.858	26.8	26.161	30.5	32.426	34.2	39.966
19.5	16.834	23.1	20.984	+26.9	26.316	30.6	32.612	34.3	40.190
19.6	16.939	23.2	21.111			30.7	32.800	34.4	40.414
19.7	17.044	23.3	21.239	+27.0	26.470	30.8	32.988	34.5	40.640
19.8	17.150	23.4	21.367	27.2	26.626	+30.9	33.176	34.6	40.866
+19.9	17.256	23.5	21.496	27.2	26.783			34.7	41.094
		23.6	21.626	27.3	26.940	+31.0	33.366	34.8	41.323
+20.0	17.363	+23.7	21.757	+27.4	27.099	+31.1	33.557	+34.9	41.553

TABLE XV.

CONDUCTIVITY OF THE ELECTROLYTES WHICH ARE MADE USE OF IN THE TECHNICAL ELECTROLYSIS OF WATER.

The table is for the temperatures of the solutions of 18° C.

P = Percentage by weight of the anhydrous electrolyte in 100 parts of the solution.

η = Number of gram-equivalents in 1 cc. of the solution; in the calculation of the gram-equivalents and litres $m = 1000$, n = the concentration, or $v = \frac{1}{m}$ the dilution.

s = Specific gravity of the solution between 15° and 18° referred to water at 4° C.

x_{18} = Conductivity in $\frac{1}{\Omega \text{ cm}}$ at 18° C.

The temperature coefficient gives in terms of x_{18} the alteration of x for +1°, and indicates the mean change between 18° and 26°.

Interpolated values are enclosed in brackets.

Electrolyte.	P.	1000 η (m; $1/v$)	$s t/4$.	$10^4 x_{18}$.	$\frac{1}{x_{18}}\left(\frac{dx}{dt}\right)_{22}$
	%	g-Eq. in l.	$t = 18°$		
Na_2CO_3	5	0.991	1.0511	451	0.0252
	10	2.082	1.1044	705	0.0271
	15	3.277	1.1590	836	0.0294
			$t = 15°$		
K_2CO_3	5	0.756	1.0499	561	0.0221
	10	1.579	1.0919	1038	0.0212
	20	3.448	1.1920	1806	0.0210
	30	5.641	1.3002	2222	0.0219
	40	8.198	1.4170	2168	0.0246
	50	11.157	1.5428	1469	0.0318
			$t = 18°$		
H_2SO_4	5	1.053	1.0331	2085	0.0121
	10	2.176	1.0673	3915	0.0128
	15	3.376	1.1036	5432	0.0136
	20	4.655	1.1414	6527	0.0145
	25	6.019	1.1807	7171	0.0154
	30	7.468	1.2207	7388	0.0162
	35	9.011	1.2625	7243	0.0170
	40	10.649	1.3056	6800	0.0178
	(45)	12.396	1.3508	6146	0.0186
	50	14.258	1 3984	5405	0.0193
	(55)	16.248	1.4487	4576	0.0201
	60	18.375	1.5019	3726	0.0213
	65	20.177	1.5577	2905	0.0230
	70	23.047	1.6146	2157	0.0256

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[1] Taken from Kohlrausch and Holborn, "Das Leitvermögen der Elektrolyte, 1898. Teubner, Leipzig.

TABLE XV—(*Continued.*)

Electrolyte.	P.	$1000\,\eta$ $(m\,;\,1/v)$	st_4.	$10^4\,x_{18}$.	$\frac{1}{x_{18}}\left(\frac{dx}{dt}\right)_{22}$
	%	g-Eq. in l.	$t = 18°$		
H_2SO_4	75	25.592	1.6734	1522	0.0291
	80	28.25	1.7320	1105	0.0349
	85	30.90	1.7827	980	0.0365
	90	33.34	1.8167	1075	0.0320
	95	35.58	1.8368	1025	0.0279
			$t = 15°$		
NaOH	2.5	0.641	(1.0280)	1087	0.0194
	5	1.319	1.0568	1969	0.0201
	10	2.779	1.1131	3124	0.0217
	(15)	4.381	1.1700	3463	0.0249
	20	6.122	1.2262	3270	0.0299
	(25)	8.002	1.2823	2717	0.0368
	30	10.015	1.3374	2022	0.0450
	(35)	12.150	1.3907	1507	0.0551
	40	14.400	1.4421	1164	0.0648
	42	15.323	1.4615	1065	0.0691
			$t = 15°$		
KOH	4.2	0.777	1.0382	1464	0.0187
	8.4	1.612	1.0776	2723	0.0186
	(12.6)	2.508	1.1177	3763	0.0188
	16.8	3.467	1.1588	4558	0.0193
	(21.0)	4.491	1.2008	5106	0.0199
	25.2	5.583	1.2439	5403	0.0209
	(29.4)	6.744	1.2880	5434	0.0221
	33.6	7.978	1.3332	5221	0.0236
	(37.8)	9.292	1.3802	4790	0.0257
	42.0	10.695	1.4298	4212	0.0283

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