

from burning does not run quite so high, it does not seem to be any more constant and the results do not seem to justify the extra weighing. It is possible that in a coke laboratory analyzing a fairly even product, a constant blank might be found and deduced, saving the extra heating and weighing.

The writers wish to acknowledge the valuable suggestions of Dr. P. W. Shimer, of Lafayette College, Easton, Pa., and to thank for their kindness Mr. W. H. Blauvelt, of the Semet Solvay Co., of Syracuse, N. Y. and Mr. G. H. Caperton, of the Fire Creek Coal and Coke Co., West Virginia.

REVIEW.

SOME RECORDS OF PROGRESS IN APPLIED CHEMISTRY.¹

The year just passed has been remarkable for the extension which the industry has undergone rather than for the development of new processes or products. Everywhere demand for products has grown and production has responded to meet it. In the United States this is particularly marked, and it is illustrated in the statistics of the imports and exports of raw materials used in the chemical arts, and of the finished product. Materials needed in the industry in this country, but not produced, or capable of production here, have been brought here in increased quantities, while the finished products have been exported in much the same ratio. We may select for illustration a few products representing the larger industries, and therefore, most widely affecting the general welfare, quoting aggregate values of the various imports.

	1897.	1898.	1899.
Alizarine products.....	\$1,022.970	\$ 886,332	\$ 700.485
Coal-tar colors and dyes ...	3,196.478	3,689,214	3,799.353
Glycerine	1,182.099	774,709	1,024,131
Calcium chloride.....	1,375.560	1,422,920	1,159,271
Potassium chlorate	458.095	308,458	173,488
Caustic soda.....	1,147.763	476.032	252.291
Sal soda.....	82.695	40.266	20.905
Soda-ash	1,241.321	589,714	310,742

If on the other hand we consider the products exported, we find a like favorable state of affairs:

¹ Read before the New York Section, October 6, and November 10, 1899.

	1897.	1898.	1899.
Acids	\$ 102,483	\$ 115,050	\$ 207,247
Copper sulphate	415,717	1,173,186
Dyes and dye-stuffs.....	450,009	442,967	478,582
Calcium acetate	537,586	700,000
Medicines	2,287,744	2,460,669	2,661,008
Fertilizers	5,005,929	4,359,834	6,964,305
Glucose.....	2,736,674	2,871,839	3,624,890
Glue.....	132,581	209,441	222,072
Gunpowder and explosives ..	118,001	139,644	182,142
Glass	1,208,187	1,211,084	1,503,651
Ink, printers' and other.....	162,995	203,927	210,973
Leather.....	9,920,851	11,251,851	13,444,569
Naval stores, rosin, tar, etc..	9,214,958	9,155,144	9,982,955
Oil cake	9,611,044	12,581,534	14,531,142
Animal oils	643,924	502,332	704,127
Cottonseed oil.....	6,897,361	10,137,619	12,077,519
Paints	944,536	1,079,518	1,447,425
Paraffin and paraffin wax....	4,957,096	6,030,292	6,804,684
Tallow.....	2,782,595	3,141,653	4,367,356
Lard	20,126,485	39,710,672	42,208,462
Lard compounds.....	857,708	1,118,659	1,200,231
Oleo oil and oleomargarine..	7,214,917	8,290,710	9,693,362
Soap.....	1,136,880	1,390,603	1,457,610
Wood alcohol.....	140,046	199,230	414,875
Starch	1,665,926	1,371,549	2,292,973
Sugar and molasses	1,708,962	2,111,658	2,953,888
Blacking.....	384,937	733,658	852,187
Candles.....	216,565	232,214	275,470
Cement.....	71,160	86,208	131,161
Coal	11,008,643	11,683,749	13,661,028
Coke	547,046	608,784	632,788

The figures of the third column are for the fiscal year ending June 30, 1899, and all are taken from the late report of the Bureau of Statistics of the U. S. Treasury Department. It would seem that no stronger or more fitting illustration of the rapid advances the chemical industries are making in the United States could be needed. And it is fair to say that what is true for the United States is true for *most* of the more highly civilized countries. The depression of the past few years has been followed by a reaction, and the increased prosperity cannot fail to bring material advances in both processes and products.

During the year important expositions illustrating the advances in the chemical industries have occurred, and among the more important the Electrochemical Exposition held in Darmstadt on the occasion of the General Meeting of the Vereins Deutscher Chemiker, and the Acetylene congresses, and expositions held in Budapest and Frankfurt. In the former, the electrolytic purification of metals was represented in Elmore and Mannesmann tubes in nickel, aluminum, zinc, tin, gold, and silver; Merck's lithium, mercury, and silicon; chemicals in ammonium and sodium persulphate, pyridine and piperidine, the products of

decomposition of alkaline chlorides, carborundum, calcium carbide; and of the highest interest though not strictly belonging to the electrical products were Goldschmidt's rarer metals produced in the works at Essen. This collection included chromium copper, chromium manganese, and copper manganese, ferro-boron, ferro-titanium, and corundum showing small rubies.

In the acetylene expositions the manufacture of carbide. the apparatus for the generation and utilization of acetylene, and processes for its purification, were shown or illustrated, and the work accomplished must be of value to the advancement of the industry. In addition to the expositions a congress was held for the discussion of the questions relating to the industry.

Dr. Borchers, of Aachen, in an address before the Deutschen Elektrochemischen Gesellschaft, presented interesting statistics showing the status of the electrochemical industry in the world, and condensed the data of his detailed table in the following :

	Power existing or projected.			Value of the possible annual production.
	Water power. H. P.	Steam power. H. P.	Gas power. H. P.	
Africa—Transvaal	454	\$ 7,224,000
America—Canada	1,500	112,500
" United States	72,300	11,750	2,500	97,506,440
Europe—Belgium	1,000	148,700
Germany	13,800	16,173	13,786,550
England	11,500	8,150	20	2,270,900
France	110,140	1,300	11,277,835
Italy	29,485	2,418,750
Norway	31,500	1,837,500
Austria	27,000	23	2,741,962
Russia	29,000	2,202,500
Switzerland	38,950	3,153,162
Spain	7,100	687,270

In the United States the quantities and values of the several products resulting from the industrial applications of electricity are as follow :

Product.	Quantity.	Value.
Aluminum	11,000,000 lbs.	\$ 2,625,000
Gold	154,000 oz.	4,900,000
Copper	150,000 tons.	56,250,000
Silver	49,280,000 oz.	28,350,000
Potassium chlorate	330 tons	54,037
Caustic soda	5,120 "	195,840
Chloride of lime (bleaching-powder)	11,200 "	230,000
Calcium carbide	60,000 "	4,500,000
Carborundum	560 "	140,000
Nickel	182.5 "	114,062

Borchers estimates from the results obtained in various locali-

ties that one effective horse power will yield by the various electric and electrolytic processes per annum,

16 tons	copper :
22 "	silver :
1.6 "	70 per cent. caustic soda, besides 3.5 tons. 38 to 40 per cent. chloride of lime :
1.8 "	80 per cent. caustic potash, besides 3.5 tons. 30 to 40 per cent. chloride of lime :
0.5 ton	potassium chlorate ;
1.0 "	calcium carbide ;
0.6 "	carborundum.

Of aluminum, one horse power will yield per annum, with

Volts.	Kilograms.
3	723
4	543
5	434
10	217

In 1897 we took occasion to call attention to the discussions in progress in Germany regarding the education of chemists for technical work giving expression of views concerning the requirements. The ideas there expressed have been developed in more concrete forms in the admirable presidential address of Mr. George Beilby, before the London Section of the Society of Chemical Industry in April of the present year. In his address Mr. Beilby discusses most intelligently and thoroughly, and from a practical standpoint, the educational requirements of the chemical industries, and he expresses these most clearly when he says "the scientific bases must clearly be a thorough knowledge of the principles of chemistry, physics, dynamics, and mechanics, and added to this there must be a practical acquaintance with materials of construction and the methods by which they are worked into structures. The ideal chemical engineer ought to be in thorough sympathy with the modes of thought and with the methods of working of both the chemist and engineer."

Following this idea, so comprehensive and so appropriate he offers "An Outline Synopsis of Chemical Engineering" which is in every way worthy of the most careful study and consideration of teachers of applied chemistry in our technical schools. It covers splendidly the needs of the industry not only for the present but the future ; for it will be seen that Mr. Beilby would provide first of all *chemists*, thoroughly educated in all the fundamental principles of the science. After that he would have them thoroughly familiar with the means whereby the principles of the science are to be applied in a large way. Following this admirable idea, his plan for the education of the chemical engineer would cover :

First. The scientific groundwork and fundamental principles.

Second. The materials of construction and the methods of working them.

Third. The special forms of apparatus used in the various kinds of operations.

Fourth. The general principles on which a chemical work ought to be planned and laid out.

Fifth. Works, management, and organization and manufacturing, profit, and loss.

When the plan of Mr. Beilby has been realized, we may expect that advances in the chemical industry, will receive an impulse from which most important results will flow.

In the metallurgical field, progress seems to have been in the direction of production rather than processes as has been noted in other fields of activity. The cyanide process for extraction of gold is being widely applied and it is said that forty works are being operated with it in the United States. The Peletan Clerici process dissolves the finely divided gold with cyanide solution and precipitates the gold in the same vessel by electrolysis using a mercury cathode. The yields quoted are 68.7 to 77.6 per cent. in one locality and eighty-five per cent. in another.

The mercury cyanide process of Keith uses a solution containing 0.05 per cent. of potassium cyanide and 0.025 per cent. of mercuric cyanide and precipitates the gold by electrolysis upon amalgamated plates. The Sulman-Teed process leaches out the gold with cyanide solution containing cyanogen bromide and precipitates the gold with zinc, the principal requirement being that the weight of the cyanogen bromide must be equal to one-fourth that of the cyanide. The yield in extraction by this process is claimed to be ninety per cent.

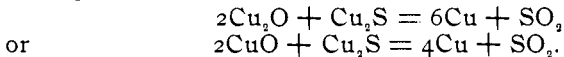
Etard proposes to extract gold with a dilute solution of muriatic acid and permanganate or the manganates of potassium or sodium and precipitates the dissolved gold with ferrous sulphate. No details of yield are given.

Smith subjects the ores to the action of nascent chlorine produced electrolytically. The ores to be treated are fed into a horizontal cylinder of wood, divided into two compartments by a porous partition, one part being lined with carbon which constitutes the anode. In the other compartment is a cathode of carbon. The ore is charged into the carbon-lined compartment with a solution of salt and the apparatus set in motion. The current is applied, chlorine is produced, and it attacks the gold present, producing aurous chloride. This substance is decomposed in the cathode compartment and the gold is deposited as a fine brown powder. Cowper-Cowles separates the solution from the ore and the gold electrolytically, using aluminum for cathodes instead of lead as recommended by Siemens. He claims that

the gold adheres better, is more easily removed, and the solution is kept cleaner. The gold is not contaminated with lead and need not be cupelled.

Tomasi has further developed his process for desilverization of lead by electrolysis. A rectangular cell enclosing fixed anodes is used and between these anodes of crude argentiferous lead is found the cathode consisting of a disk of aluminum bronze which may rotate at the rate of one to two turns per minute. Only a portion of the disk is immersed in the electrolyte which consists of lead and potassium acetate. The finely divided lead is removed from the cathodes by brushes and collected. The silver falls as anode mud. The physical condition of the lead obtained is most favorable for oxidation.

In the extraction of copper the Herreshoff progressive and continuous roasting furnace has attracted the most favorable attention. It consists of a vertical cylinder divided into sections by horizontal diaphragms, the alternate diaphragms having openings at the center and periphery, respectively, the ore being moved forward and downward by properly arranged rakes the arms of which are attached to a vertical shaft passing through the middle of the cylinder. James and Nicholls, of Swansea, carefully roast the properly concentrated ore and transfer it to a second roasting furnace where it is mixed with a given quantity of fresh unroasted concentrate whereby the copper oxide of the first operation is reduced in accordance with the following :



They claim saving of time, labor, furnaces, loss of noble metals: a high yield of copper, very pure sulphurous gas. Keller considers the purity of the copper obtained not greater than that from the reverberatory furnace process and below that of the Bessemer process.

The Hoepfner process for extraction of copper seems to be extending notwithstanding the unfavorable criticism. It is stated that new works at Papenburg will extract daily about 1000 kilograms of copper. The ore is finely pulverized in a Krupp mill, leached with copper chloride solution, the copper, lead, nickel, and silver extracted, while the cupric salt is reduced to the cuprous condition. The solution is purified, freed from silver, and caused to flow through compartments having carbon anodes and copper cathodes. The chlorine separating at the anode is taken up by the copper solution and the regenerated cupric liquor is heated and returned to a new lot of ore. From Rio Tinto ores with 3.37 per cent. of copper, ninety-one per cent. of the metal was recovered after four hours' treatment and only three per cent. of the iron content dissolved, while by a longer extraction

period 98.5 per cent. of the copper is secured and only four per cent. of the iron taken up. It is claimed for this chloride process that with eight-tenths of a volt ninety per cent. of the current is utilized so that one horse power in twenty-four hours will produce fifty-four kilograms of copper against fifteen kilograms by the sulphate process. Hoepfner claims that by this process the electrolytic recovery of lead, nickel, silver, and zinc has been solved, and discusses the modifications in the process involved.

In the extraction of nickel the process of Mond has been further developed by the construction of extensive works at Southwick in England. The product from the Bessemer process is used. It is first roasted and then contains thirty-five per cent. of nickel and forty-two per cent. of copper, and about two per cent. of iron. The nickel content is then increased to fifty-one per cent. by extraction of part of the copper with vitriol, the residue then transferred to the vertical plate furnace, and the copper and nickel reduced with water-gas hydrogen at a temperature not above 300° C. without reducing the iron. The nickel is now volatilized below 100° C. as the carbonyl compound in the plate tower. After a time the residue is returned to the reducing tower, and thus wanders back and forth between both ovens seven to fifteen days when sixty per cent. of the nickel will have been removed. The carbonyl compound is decomposed at 180° C. and the nickel deposited on iron plates or in a granular condition, while the carbon monoxide is returned to the furnace. The metal obtained contains 99.8 per cent. nickel and it is claimed that the process may compete with others for the extraction of the metal.

Storer's method seems to have the attraction of being inexpensive and simple. He treats ores containing silicate, hydrate, or oxide of nickel with ferrous chloride solution,—one part of ore with 2.75 parts of solution containing 26.5 parts of the iron salt,—in a closed vessel heated to 187° C. with live steam and with corresponding pressure. After five to eight hours' digestion, and double decomposition has been effected, the vessel is emptied, the iron oxide produced is collected, and washed to be used as pigment, while the nickel may be separated from the solution by electrolysis or by precipitation. About 750 pounds of ferrous chloride are consumed per ton of ore.

The metallurgy of zinc has been practically stationary. Jones subjects the ore to oxidizing and roasting, leaches the ore with water or weak acid, separates the iron with ammonia, filters and electrolyzes in a cell with a diaphragm, adding ammonium sulphate to the anode space. Kohler heats the roasted and oxidized ore with ammonium sulphate, leaches the residue, and precipitates the solution to recover the zinc as hydrate. Bechi mixes the ore with "Abraumsalz" or common salt and roasts the mixture.

Then he leaches the residue, heats the solution with zinc hydrate, whereby copper is precipitated and zinc chloride left behind. This latter may be decomposed by lime, or the zinc may be separated by electrolysis. Schultz finds that zinc chloride ordinarily electrolyzes with difficulty and that presence of water is unfavorable. He evaporates the solution almost to dryness and mixes with strong hydrochloric acid, when, it is declared, electrolysis becomes easy and the deposit fine.

The process of Goldschmidt for obtaining high temperatures and the reduction of refractory metallic oxides by combustion of aluminum has been further developed. The aluminum used must be finely divided and intimately mixed with the oxide to be reduced. The mixture is ignited by adding a strongly oxidizing agent such as barium dioxide and after being started may be made continuous. The alumina slag solidifies as corundum and may be used as abrasive material or for the manufacture of aluminum. The method is employed for production of alloys and for welding. For the latter purpose an impure aluminum serves perfectly well. Kupfelwieser has made a careful study of the method of Goldschmidt. He finds the heat of combustion of aluminum to be 7140 calories and gives the following data representing the requirements for production of one kilogram of:

	Iron.	Manga- nese.		Sili- con.	Chro- mium.	Tung- sten.
Compound used.....	Fe ₂ O ₃	MnO ₂	Mn ₂ O ₃	SiO ₂	Cr ₂ O ₃	WO ₃
Aluminum required.....	0.484	0.656	0.492	1.272	0.520	0.294
Heat developed, calories.	3456	4684	3512	9082	3712	2099
Heat consumed :						
(a) for reduction.....	1796	2115	2000	7830	2200	1100
(b) for melting slag....	548	742	550	1439	582	324
(c) for melting metals..	362	535	535	435	434	360
Total heat used.....	2706	3392	3091	9704	3216	1784
Excess to cover losses, etc.	750	1292	421	672	497	315

Silicon has been produced in the electric furnace. Hyde has thus produced the crystalline and graphitoidal form, and so likewise has De Chalmot. The latter obtains a mixture of copper, silicon, and copper silicide. The copper is separated with nitric acid and the liberated silicon freed from silica with hydrofluoric acid. The Fabrik Elektrometallurgischer Produkte zu Frankfurt-Bockenheim, have, by a secret process, brought into the market rods of silicon which they specially recommend for use in manufacture of iron and steel. In iron it increases the graphite, reduces the shrinkage of castings and the tendency of liquid iron to absorb gases. For low carbon steel it is desirable because it effects the necessary reductions without introducing carbon. The same firm offer copper silicide in eight to nine kilogram bars, containing ten, fifteen, and thirty to thirty-five per cent. of

silicon. This compound serves for deoxidation of copper instead of copper phosphide. Silicon increases the strength but reduces the conductivity of copper containing it. These relations are as follows:

	Strength per square millimeter. Kilograms.	Con- ductivity.
Pure copper.....	28-35	100
Copper with 0.5 per cent. silicon	50	28
Copper with 3.5 per cent. silicon.....	95	7

But the compound is useful in the form of bearing metal, strong wire, and sheet, for resisting acid gases and vapors.

The production of phosphorus in the electric furnace has been extended, and this is not the only application of the current to high temperature distillations. Several forms of furnace have been devised for heating materials with exclusion of air and with reducing media, together with condensation and collection of the volatilized products. Many attempts, more or less successful, have been made both in this country and abroad to apply them to the production of phosphorus. In most cases the calcium phosphate is heated with excess of carbon, liberating the phosphorus and leaving calcium carbide behind. In other cases, as in the furnaces of Albright and Wilson, the phosphate is mixed with sand as well as carbon. Harding makes a tolerably pure phosphoric acid, and this, mixed with carbon, is charged to an electric furnace with an outlet at one side for slag. A hollow electrode projecting through the bottom is connected with a carefully controlled supply of volatile hydrocarbon, such as gasoline, and the phosphorus liberated and volatilized is carried off through a pipe at the top of the furnace. Hasenclever discussing the progress in sulphuric acid manufacture in 1898 calls attention to the improvements made by the Badische Anilin und Soda Fabrik in the application of the contact reaction of Winkler, whereby combination of sulphur dioxide and oxygen is effected by passing the gases over platinized asbestos or pumice. They found that the heat generated by the reaction tends to so heat the after-end of the contact mass as to cause it to induce a reverse reaction and the reduction of the sulphur trioxide to the dioxide. To prevent this they cool the contact mass either by currents of air or gases about it, or by baths of fused metal, and the cooling is so carefully controlled that the reaction is practically quantitative. Besides the very much larger yield obtained, injury to the apparatus, and weakening of the contact mass are diminished.

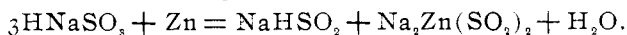
Another important requirement of the successful application of this reaction is that the gases shall be free from dust and injurious impurities such as arsenic, phosphorus, mercury, etc. If washed with water, the gas must subsequently be dried, and it must be chemically and optically free from dust.

Meyer proposes the use of cylindrical instead of rectangular chambers in the manufacture of sulphuric acid, and recommends spiral circulation of the gases. In the application of the idea the gases from the Glover tower are made to enter tangentially at the periphery of a vertical cylindrical chamber and at about midway between the top and bottom. Circulating about they pass out at the center of the bottom and pass along to other chambers which may be similarly cylindrical or of the rectangular form. The outlet, to provide against destruction of lead connections which had been found to occur, is of stoneware of special construction, and to increase the cooling surface a cylinder is let into the center of the top of the chamber, and circulation of air induced by an open pipe hanging within the cylinder. The air flows down through the annular space thus made and up through the pipe. Numerous economies are claimed for the system.

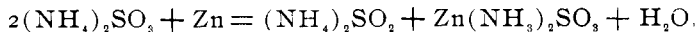
Hydrogen sulphide is formed in considerable quantity as a by-product in asphalt refining in the works of the California Asphaltum Works at Ventura, California. It is burned to sulphur dioxide, and this in turn is converted in chambers in the usual way to vitriol yielding daily ten tons of finished acid of very high purity.

Mourlot produces magnesium sulphide in the electric furnace by heating together, in molecular proportions, magnesium chloride and tin sulphide, with a current of 50 volts and 2000 amperes. Tin chloride is formed and volatilized while magnesium sulphide remains, partly or wholly fused. The latter product is not attacked by the carbon of the anode, is less sensitive to the action of water than the powdery form which decomposes suddenly under such influence, but in the presence of steam, it breaks up quickly with formation of magnesium oxide and hydrogen sulphide.

It is well known that when an acid sodium sulphite is treated with zinc, three molecules enter the reaction and sodium hydro-sulphite and double sulphite of sodium and zinc are formed.

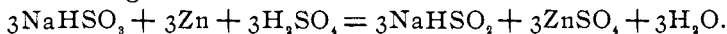


But Prudhomme finds that if ammonium bisulphite solution be neutralized with ammonia, and the whole poured over zinc, the reaction, as written by him, becomes :



The zinc salt is insoluble and may be separated by filtration. The advantages of this reaction are : direct formation of a neutral salt less easily oxidized than the acid salt with ninety-six to ninety-eight per cent. of the theoretical yield ; utilization of half the bisulphite treated ; production of neutral hydrosulphite free from zinc salt by simple filtration.

Grossmann's process is still more economical as regards consumption of bisulphite. Taking a solution of the salt of 60° Tw. and containing twenty per cent. of total sulphur dioxide, he mixes it with sulphuric acid and zinc dust in accordance with the following reaction :



He found that the liquor so produced has three times as much reducing power as the ordinary zinc bisulphite bath in indigo-dyeing and considers it a distinct improvement upon the bath heretofore used.

The electrolytic production of chlorine and its compounds has undergone considerable increase during the past year. Hasenclever says the extension of electrolytic chlorate manufacture both in Sweden and French Switzerland has been so active that the price has fallen in Germany from 100 to 120 marks per 100 kilograms to about 55 marks, and that many manufacturers have resorted to manufacture of other products particularly carbide.

Production of chloride of lime has grown to such an extent that increasing quantities are available for export. John Brock, president of the United Alkali Company, stated to the stockholders that while in 1895 the export of soda from England to America was 125,698 tons, it had fallen to 29,393 tons in 1898. During the same period caustic fell from 33,625 to 11,171 tons, and chloride of lime suffered in the same way. The company had established works at Bay City, Michigan, to supply the American market under the title, The North American Chemical Company.

The National Electrolytic Company, of Niagara Falls, now use 1100 horse power supplied by the Niagara Falls Hydraulic Power Company in the production of potassium chlorate, using the process of W. T. Gibbs applied to potassium chloride from Stassfurt. They are now doubling their works.

The cell and diaphragm of Hargreaves and Bird have at last been authentically described. The cell is made up of two parts, the anode compartment and the cathode space. The former consists of a leaden box, pitched inside and further lined with a wall of Portland cement. Bolted to each side of this is a cast-iron box which encloses the cathode space. If the cell be horizontal, only one cathode space is provided and constitutes the bottom. The anodes consist of rectangular carbon slabs which are arranged parallel with each other, the edge of one overlapping that of the other, forming a sort of horizontal grating in the horizontal cell and sustaining walls in the vertical ones. The anodes project through the one wall and rest in depressions in the other, the outer ends being covered with lead or type metal connected with each other by metallic conductors. Between the

anode and cathode spaces is the cathode diaphragm peculiar to the Hargreaves cell. It consists of iron gauze upon which has first been floated paper or asbestos pulp. This is covered with Portland cement in moist thin layer, and for protection this in turn is covered with porous fibrous material such as asbestos cloth, wool, or other similar substances. For easier removal of the product the layer next the gauze is impregnated with some soluble substance which, in the first operations, washes out, leaving narrow spaces about the wires of the cathode.

When the cell is set up the anode space is filled with the electrolyte solution, and solid electrolyte (salt) is fed in through an opening in the top which is closed, when the cell is in operation, by a stoneware lid resting in a water seal. In the horizontal cell the solid electrolyte rests upon the anodes and in the vertical cell is held between the two rows of anodes. Inlets and outlets are provided for the circulating electrolyte solution, and for exit of chlorine. If the solid electrolyte contains too much insoluble impurity it is dissolved in a separate vessel through which the liquid electrolyte is made to circulate. Steam is fed to the cathode space and the caustic dissolved flows out through the bottom.

One of the criticisms of the Hargreaves cell has been that the alkali produced is contaminated with salt. This difficulty has been overcome by the application of the fact observed by Hargreaves that when salt solution containing but little sodium carbonate is evaporated, the carbonate content increases and the mother-liquor contains salt and carbonate in the molecular ratio of 2 : 1 ; and furthermore that on boiling salt crystals or a crystal mixture of salt and carbonate (the monohydrate) with a large quantity of concentrated soda solution, the salt will be dissolved and separated from the monohydrate. Hargreaves has devised a system of pans and crystallizing vessels for effecting such separation.

The method of circulation of the cathode mercury of the Castner-Kellner cell has been the subject of modification at the hands of several inventors with more or less advantage. G. and G. W. Bell having in view both this and the saving of cell space, erect three columns of shallow trays, the trays of the middle column being much larger than those of the other two columns. Communication is established between the trays of the middle column and those of the same level of the outer columns respectively in such a way that when the cells are charged with mercury a perfect seal between them is established. Inlets and outlets for circulation of electrolyte in the outer series of cells is provided, and each anode cell has likewise an outlet for chlorine communicating with a general conduit. The cells are firmly held together by bolts passing vertically through all. The anodes

project horizontally through the anode cell walls, each tray being provided with the necessary anodes. Water is fed to the trays of the middle column and may be caused to circulate. With the apparatus properly set up, charged with mercury and electrolyte and the current operating, the chlorine outlet of one series of anode cells is partly closed and pressure thus generated within the cells drives the mercury toward the other columns. After a proper time this outlet is opened, the pressure released, the outlet of the other column partly closed, and the current of mercury reversed. The mercury is thus made to oscillate back and forth between the anode cell and the so-called cathode cell, but really the decomposition cell, and the reaction completed.

The Electron Chemical Works effect a circulation of the mercury by means of a steam injector, whereby the mercury is atomized or pulverized in contact with steam. The latter is decomposed by the alkali metal, an excess being condensed to dissolve the hydroxide produced. The mercury is led back to the electrolytic cell by gravity and the circulation thus maintained.

To obviate the difficulty arising from the diffusion of the anode and cathode products in apparatus having a mercury cathode, the Solvay Company resort to superposed strata of electrolyte of different densities and maintain these densities by careful circulation of the liquid of the strata through boxes containing the solid electrolyte. Vertical diaphragms across the ends of the cells and extending to different depths serve to establish the layers and the circulation of the strata of liquid is maintained by pumps.

Acker decomposes fused salt over melted lead, producing chlorine and sodium lead alloy. The furnace consists of two concentric cylinders of magnesite. The inner cylinder really constitutes a bell hanging within the outer cylinder. The bottom of the furnace is of iron, and the cathode passes through it. Fused lead is fed through the bottom until the mouth of the bell is sealed and the current is applied while the anodes within the anode space is in contact with the lead. These are withdrawn until an arc is produced, and salt is instantly charged to the annular space. Chlorine is generated and is led away through an outlet provided for it, and the sodium liberated combines with the lead. The alloy, which is lighter than the metal rises within the bell and overflows through a tube passing out at the bottom. No data regarding the operation and efficiency of the furnace are given.

Muspratt and Smith find that the requirements of successful operation in manufacture of high strength hypochlorite solution, are: Continued excess of alkali in solution, low temperature, below 80° F., a gravity of solution at which salt deposits most readily, prompt and complete removal of scum if present, and periodical introduction of caustic. The stability of the product

depends upon the absence of iron and the maintenance of such strength that salt does not deposit. The authors declare that under favorable conditions, solutions containing thirty-five per cent. by volume of available chlorine may be made, and such a solution is, excepting unmerchantable strengths of hydrogen peroxide, the strongest oxidizing agent known.

It has been found that electrolytic chlorine does not give a good yield of chloride of lime, and Sindig-Larsen ascribes this to the fact that electrolytic chlorine is more active than that produced by chemical methods and believes that the oxygen is replaced producing calcium chloride. To avoid this he carefully dries the gas by passing it over calcium chloride, and then heats it by passing it through tubes heated to 700° or 800° C. Then it is cooled and passed into the lime chambers in the usual way.

Dr. Erich Muller finds that the efficiency of electrolysis in the production of oxidized salts of chlorine, bromine, or iodine, is greatly enhanced by the addition of a small proportion of potassium dichromate. Thus with a thirty per cent. salt solution he obtained 32.8 per cent. current efficiency, while with a similar solution under practically like conditions, but containing 0.18 per cent. of potassium dichromate, he secured 69.6 per cent. of current efficiency. The current efficiency in the production of iodate was ninety-seven per cent. while 97.6 per cent. of bromide was converted to bromate corresponding with ninety-four per cent. efficiency.

Meister, Lucius, and Bruning oxidize chromous salts by electrolysis in presence of sulphuric acid with a current of three and five-tenths volts, and 300 amperes and a temperature of 50° C. The operation is carried out in a leaden vessel with a diaphragm. When the anode liquid is fully oxidized it is removed and the cathode liquid transferred to the anode cell and the cathode cell filled with fresh solution. To obtain the best results a solution of high conductivity is recommended and the proportion of 100 grams of chromic oxide, and 350 grams of sulphuric acid seem to meet this condition.

The Neustassfurt Salt Works oxidize manganate to permanganate by electrolysis in a vessel in which the cathode cells filled with water are suspended in the anode liquid in which the manganate is dissolved. Upon application of the current the manganate is oxidized and potassium hydroxide is liberated in the cathode cell. When the strength of the hydroxide reaches forty per cent. the permanganate is nearly insoluble, and precipitates. To maintain the proportion of manganate this salt is suspended in the anode liquid in vessels with perforated bottoms. The process may be made continuous.

To prepare oxygen, Stewart fuses a mixture of sodium

manganate and hydroxide, the proportions of the constituents being such that fusion occurs at 375° to 400° C. The fusion is effected in cast-iron vessels and air is passed through the mass. When, after a few minutes, absorption of oxygen is complete, air is cut off and steam admitted. Oxygen is promptly evolved and decomposition is soon complete. The operation is then reversed. Four retorts, two feet square and eight feet long, are said to have a capacity of 140 to 150 cubic feet of oxygen daily. Hitchcock declares that when oxygen is used with bleaching-powder the efficiency of the latter is increased, and a saving of thirty to forty per cent. is effected.

Ladenburg condenses ozone by cooling it with liquid air and fractional distillation of the ozonized oxygen. Oxygen passes off until the volume is reduced to ten per cent. when evaporation ceases. The product thus obtained has a dark blue color, contains 86.14 per cent. of ozone and has a density of 1.3698 compared with oxygen. From this the density of ozone was found to be 1.456. The liquid ozone boils at -125° C. but at once explodes violently.

The commercial production and utilization of ozone is extending. Kershaw discusses the more recently improved forms of apparatus for the purpose and particularly those of Andreoli, Otto, Yarnold, and Siemens and Halske, describes their construction and operation and presents data of yield obtained and cost of energy employed to produce one kilogram of ozone and active oxygen respectively as follow :

Form of ozonizer.	Yield of ozone per E. H. P. hour Grams.	Cost of electrical energy per kilo of ozone.	per kilo of active oxygen.
Yarnold	175	\$0.57	\$0.513
Otto.....	150	0.20	0.60
Andreoli	94	0.30	0.954
Siemens and Halske	20	1.50	4.50

According to Kershaw ozone produced by the apparatus of Yarnold, Otto, and Andreoli is three to four times as expensive as bleaching-powder and about fifty per cent. more expensive than sodium bichromate, as a source of active oxygen. Engledue places the cost of ozone produced by the Yarnold apparatus at about five and one-fourth cents per pound, of active oxygen at about fifteen, and of one electrical horse power at two cents. The successful production of ozone requires absence of heating in the apparatus and that the air to be ozonized shall be thoroughly dry and free from dust. Engledue proposes many uses of ozone including bleaching of oils and in this latter is supported by Ronco who declares that in the practical operation, the cost of handling, daily, five tons of oil effectively, was 45 francs. Andreoli recommends purification of water with ozone and states

that after treating water containing from 6,000 to as high as 110,000 microorganisms per cubic centimeter, in eleven trials, no active organisms remained; in ten other trials ten organisms per cubic centimeter were found, and the largest number found after four other trials was forty.

The production of liquid air is progressing and it is fair to believe that it will find practical applications. A company has been established in New York City for the manufacture of liquid air and claim a daily capacity of 1,500 gallons. Facts regarding cost of the product are not easily obtainable but there is reason to believe that it can be produced at low expense.

Hempel declares that with Linde's machine, one horse power hour will yield one cubic meter of air containing fifty per cent. of oxygen. He states that though its chemical uses thus far have been confined to making an explosive by mixing with carbon, and to producing chlorine in the Deacon process, it should also serve a useful purpose in making producer gas whereby, in the product, the carbon monoxide, marsh-gas, and hydrogen would be increased about 100 per cent. and the nitrogen reduced to a corresponding extent. It should also be used for increasing the efficiency of combustion of ordinary fuels, in the operation of gas engines, in connection with the Bessemer process and in the manufacture of sulphuric anhydride by the contact process. He would furthermore use the nitrogen in a concentrated state for the production of nitrides and cyanides.

In the past couple of years the production of white lead has received marked attention and many new and promising processes of manufacture have resulted. Beilly, Cox, and Hey volatilize the metal in an electric furnace, subject the vapor to the action of air and steam, carbon dioxide, and acetic acid. The resulting reaction occurring is said to yield white lead of high quality. Cook and Clark on the other hand subject finely divided lead to the action of water and air and claim production of the hydroxide. This is separated by levigation from the unoxidized metal and the process continued until the metal is all oxidized. The hydrate is used as such or is carbonated with gas to produce white lead. In the Mathews process the ground oxidized product is digested a short time with a solution of lead oxide in glycerine and acetic acid and the solution filtered. The filtered liquid is then treated with pure carbon dioxide to proper saturation, the fine white precipitate of basic lead carbonate separated and washed in a filter press. The mother-liquor and washings are returned to the beginning of the operation. The cake from the filter-press is carefully dried and is in such condition that mill-grinding is not needed. The solution contains seven to seven and a half per cent. of glycerine and this seems essential to the proper precipitation of the

product. It is claimed for the process that white lead can be produced by it at greatly reduced cost and that its color and general physical properties are superior to those of the product obtained by the corrosion process.

Galloway's process depends upon the decomposition of lead nitrate with ammonium carbonate under pressure.

The Elektrochemische Industrie Gesellschaft (Köln) have improved upon the process of Luckow. In the new process the anion of one salt serves to dissolve the anode and the anion of the other salt precipitates the dissolved metal. The first salt is present in the proportion corresponding with the highest conductivity of its solution, while the second which serves to precipitate the metal in the insoluble condition is calculated from the electrochemical equivalent related to the current strength. It is by this rule found that seven per cent. of sodium chlorate and 0.011 per cent. of sodium carbonate are the proportions of these substances in solution best suited to the electrolytic production of white lead using hard lead anodes and soft lead cathodes; ten anodes and eleven cathodes, each with a surface of twenty by thirty cm., are suspended in the solution, fifteen cm. apart. During the electrolysis, with a current of five-tenths ampere per square decimeter and one and two-tenths to one and three-tenths volt at a temperature of 15° to 17° C., carbon dioxide is carefully injected into the solution through fine jets for the regeneration of the precipitation salt and circulation of the liquid.

Bradley and Jacobs have developed an interesting reaction in the electric furnace. They find that if barium sulphate be heated with a limited supply of carbon, part of the sulphate is reduced to sulphide and the sulphide reacting upon the residual sulphate converts it into oxide with the production of sulphur dioxide. The oxidation of the sulphide is not complete and the product in actual practice contains about forty per cent. of sulphide.

To avoid glazing the surface of barium carbonate when heating it to prepare barium dioxide, Feld encases the furnace with iron and uses fuel producing no vapor of water in burning, thus excluding all moisture from the furnace. Knoop renders phosphorite and other similar phosphatic material citrate-soluble by heating it with silica and alkali salts, and after an extended experience finds a mixture of chalk sand and alkali sulphate with the phosphate to give the best results and to make ninety-nine per cent. of the phosphate soluble.

Mabery and Baltzley recommend the use of sodium aluminate for removal of lime and magnesia from water and claim to have removed from water ninety-eight per cent. of these substances

even when the quantity of reagent used was less than was required by theory. Their paper on the subject is to be found in the pages of this Journal.

The extension of manufacture of coke with recovery of gas and by-products is increasing both in Europe and this country. In the latter they have been established at Halifax, Nova Scotia, Boston, Mass., Glassport, Penna., Benwood, West Virginia, and Ensley, Alabama. The operation of these furnaces has been discussed by Pennock in our own Journal and by Hoffmann in the *Engineering and Mining Journal*. The latter authority states that in Halifax, where the Semet-Solvay ovens are built in groups of ten, each retort is charged with five tons of coal which is coked in twenty hours. The gas-pressure is 1.25 cm. and the temperature of the oven 1000° to 1100° C. The coal used contains about sixty per cent. of fixed carbon and the gas produced having over sixteen candle power is used for lighting and the remainder for heating. Thirty-seven tons of coal coked in twenty-four hours yields 31,000 cubic feet of gas, of which 32.26 per cent. is illuminating gas and 67.74 is power-gas. The coal contains nine and nine-tenths per cent. of water of which four per cent. is hygroscopic. The results obtained at Glassport, using Youghiogheny coal, are of interest.

Products from one long ton of coal		Pounds.	Per cent.
Coke	{ Large coke > one inch.....	66.69	71.13
	{ Small coke a half to one inch..	1.64	
	{ Breeze < one inch.....	2.80	
Tar.....		75.7	3.38
Ammonia (= 1.373 sulphate).....		7.6	0.34
Gas, total 10,390 cu. ft. of 0.466 sp. gr.		368.0	16.43
Sulphur compounds in gas.			
Hydrogen sulphide, 0.98 lb. per 1000 cu. ft.		10.8	0.48
Carbon disulphide, 0.13 " " " " "		1.6	0.07
Gas liquor and loss by difference		182.9	8.17
		2240.0	100.00

49.5 per cent. of the gas was surplus, not needed for heating the ovens. The coke contains 8.91 per cent. of ash, 1.27 per cent. volatile matter, 0.0041 per cent. phosphorus, and 3.67 per cent. water. The tar recovered is preferable to gas-tar for distillation.

Muller shows that benzene is appreciably soluble in water and that this should be taken into account when large volumes of water are used in the scrubber for purification of the gas. Absorption varied with the proportion of benzene and from about three to eight per cent. of that present. Paraffin oil absorbs practically all the benzene and is used in the determination of that present in coke-oven gas.

According to Scheithauer, if 100 cubic meters of gas from oil be compressed to twelve atmospheres, six to eight kilograms of liquid hydrocarbons are separated and the gas loses twenty-five per cent. of its illuminating power. The condensed liquid contains seventy per cent. of benzene, fifteen per cent. of toluene, five per cent. of higher homologues, and ten per cent. of ethylene homologues.

The production and utilization of calcium carbide have made some advances and many of the difficulties involved have been obviated. The subject has been discussed so clearly and with such manifestly high authority by Wolff in an address before the Berlin Section of the Vereins Deutscher Chemiker that it seems important to present here a somewhat detailed abstract of what he has set forth.

He gives Moissan the credit of being the original producer of carbide in a large way declaring that Bullier and Willson followed and made their discoveries practically simultaneously, but with no knowledge of each other's work. The industry had extended so that in the autumn of 1897 the power consumed thereby in Germany was 6,000 to 8,000 horse power, in Norway 19,000, while works are projected in the Tyrol and other localities in Austria, in Switzerland, France, and Sweden. He states that in 1897 the production amounted to 10,000 tons. Yet in spite of the wide extension of the production he expects little reduction in the price of the product. The cost depends upon three factors: 1, cost of power; 2, price of raw materials; and 3, yield. All these naturally vary greatly. Mode of operation, plans of furnaces, construction, etc., likewise influence the results. Saving of heat is one of the most important and the author commends Pictet's plan of previously heating the charge by means of gas and the oxyhydrogen flame, thus saving the current. He finds the cost of carbide at the works at Vernier, near Geneva, to be 157 francs, say, \$31.40 per ton (1000 kilograms).

Discussing the danger from explosion of acetylene, he ascribes it to two causes: 1, carelessness; 2, the chemical and physical properties of acetylene. The first cause is avoidable by bearing in mind that ordinary gas and air mixtures have explosive limits of between eight and twenty-eight per cent. while acetylene air mixtures which contain three to eighty-two per cent. of acetylene are explosive. Under ordinary pressure acetylene is not explosive. Under high pressures and liquefied it may be. His conclusion is that acetylene is no more explosive than any other burning gas; but it may be and is dangerous under false conditions and in bad apparatus.

His experience with producers leads him to recommend unqualifiedly the apparatus of Pictet in which the carbide is

allowed to fall into a large volume of water and for purification he recommends the method of Frank, subjecting the gas to the cleansing action of acid metallic salts. Yet because of the many inconveniences due to ammonia and sulphides in the gas he prefers his own; that is, washing the gas in calcium chloride solution to remove ammonia and sulphides, and then passing it over chloride of lime to oxidize the phosphorus and other compounds.

For burners he particularly recommends two of special construction based upon the Bunsen principle. The first consists of two tubes pointing toward each other at right angles, the jet from one impinging upon that from the other. The gas issues from a small aperture in a tube surrounded by four air-holes, so that the gas issues from the tip mixed with air. The other consists of a small metal tube with a slit burner of lava like ordinary gas-burners. The gas issues from a small aperture surrounded by air-holes and mixed with air issues from the slit burner. These forms prevent overheating and consequent decomposition of the gas before burning and avoids deposition of heavy decomposition products in the slit. The cost of the gas to consumers must naturally vary. Compared with illuminating gas at say \$1.20 per thousand cubic feet and acetylene at \$10.50 for the same quantity, the ratios for sixteen candle power of light become:

Acetylene.....	\$1.65
Gas, slit burner.....	3.00
Gas, Welsbach.....	0.54
Electric incandescent lamp.....	3.50

With gas at sixty-five cents per thousand, the price paid in New York at the present time, the figures for light with that substance would become 1.50 and 0.27. Under any circumstances therefore acetylene could not compete with gas in Welsbach burners but it would be less expensive than electric light.

Lewes recommends the use of acetylene in admixture with water-gas and Julius Pintsch mixes thirty-five volumes of acetylene and sixty-five volumes of oil-gas for use as illuminating material. This mixture may be compressed to six atmospheres without danger of explosion.

Pictet's method of purification of acetylene consists in passing the gas through a calcium chloride solution cooled to -20° C. and then through concentrated sulphuric acid cooled to -40° C. It gives excellent results. A. Frank uses a mixture of one part copper chloride and eight parts hydrochloric acid. Acid-resisting vessels are naturally necessary. Wolff recommends chloride of lime (bleaching-powder) mixed with chromic acid salts. Ullman recommends chromic acid alone and finds that it removes both phosphorus and sulphur. He considers it the most effective purifying agent thus far used.

Berthelot and Vielle find that when acetylene is mixed with other gases, such as hydrogen and illuminating gas, the pressure limit for explosibility approaches that for acetylene alone, and particularly as the content of acetylene grows. The law is independent of the inert gas. Emerson Reynolds made experiments on the influence of carbon dioxide on the illuminating power of acetylene. Five to eight per cent. of carbon dioxide reduces the smokiness of the flame and especially prevents clogging the burners. Increase in illuminating power was not marked, but the mixture containing five per cent. of carbon dioxide gave as much light as acetylene alone and there was, therefore, reduction of the volume of acetylene burned. Carbon dioxide probably has some oxidizing effect.

To undertake a discussion of the forms of furnace for manufacture of carbide would be impossible within the limits of this paper. The principal improvements depend upon continuity of operation, saving of heat generated in the operation by applying it to increasing the temperature of the charge or heating the charge from external sources in order to reduce the consumption of heat of the arc.

Bradley and Horry obtain more or less of continuity of operation by causing the charge to meet the electrodes in the periphery of a wheel or cylinder, so that the carbide formed in blocks at one side may be removed more or less cooled at the other side. The production of dust seems to be one of the prime difficulties occurring in the operation of this furnace.

Kenevel, Spofford, and Mead use horizontal revolving cylinders as electrodes in the bottom of a vertical shaft and so aim at continuity. Roberts feeds the charge from a hopper upon the electrodes, arranged horizontally above a movable apron or endless belt. The electrodes are brought into contact covered by the charge, the belt set in motion, the electrodes gradually separated, and the motion of the belt graduated to the speed of formation of carbide between the electrodes. The carbide lies in a bed of material of the charge and is covered with it. It, therefore, has an opportunity to cool with partial exclusion of air. Pictet heats the charge in a vertical shaft on its way down to the electrodes, nearly to the temperature of the reaction, thus saving electrical energy. His furnace is being used by the Ingleton Carbide Company in England. Memmo charges a mixture of calcium hydroxide and carbon and uses the water-gas said to be formed in the furnace for heating the charge. But these problems presented in the carbide manufacture are not easy and they still await perfect solution.

Hintz and Bunte, independently of each other, have made experiments with Welsbach mantles to determine the best mixture to use in their manufacture, to secure the highest efficiency

find that the mixture of pure thorium oxide with pure cerium oxide is best, and that the presence of other oxides such as neodymium, zirconium, lanthanum, and yttrium are rather detrimental than otherwise. They find that the efficiency of the mantles declines with the length of use, and that the consumption of gas per Hefner candle power, under the different conditions stated, is as follows :

Thorium oxide. Per cent.	Cerium oxide. Per cent.	Gas consumed during burning.		
		100 hours. Liters.	400 hours. Liters.	800 hours. Liters.
99.9	0.1	12	15	15
99.5	0.5	3.3	4.3	5.2
99.0	1.0	2.6	3.0	3.6
99.0	1.0	2.9	3.2	5.2

Other experiments gave :

Thorium oxide. Per cent.	Mixture. Cerium oxide. Per cent.	Hourly consumption for one Hefner candle power.
99	1	1.7
98	2	2.2
97	3	2.4
96	4	4.2
90	10	13.0
80	20	27-34
70	30	31-85
50	50	87-110

Bunte found that pure thorium oxide gives little light (three H. C. P.), pure cerium oxide but little more (six to seven H. C. P.), while the Welsbach mixture gives about seventy H. C. P. He explains this by the theory of Drossbach, according to whom pure thorium does not react upon light waves except in presence of a small quantity of cerium, when it becomes resonant and illuminating.

Auer von Welsbach uses a filament of osmium *in vacuo* heated by the electric current, finding that it will withstand a higher temperature than carbon. It is therefore more efficient, since incandescence increases rapidly with the temperature. When heated to volatilization of platinum it gives a most agreeable white light. The osmium may contain platinum in small quantity but it must otherwise be pure. He greatly increases the luminosity by covering the osmium filament with thorium oxide.

Nernst has further developed his incandescent lamp, the value of which depends upon the power of magnesia when heated to conduct the current, to become further highly heated by the current, and in consequence of the intense heating to become incandescent. He constructs a thin cylinder of magnesia, heats it to the temperature necessary to conduction and passes the current. The light developed amounts to one Hefner unit (0.88 English unit) per watt, against one Hefner unit to three or four watts,

with the ordinary incandescent lamp. Nernst finds that even at 1000° C. magnesia does not conduct well and that its conductivity may be increased by addition of boric acid, calcium chloride, and tungstic acid. Zirconium oxide with about five per cent. of yttrium oxide; thorium oxide with twenty per cent. of yttrium oxide; thorium oxide with thirty-seven per cent. of zirconium oxide, three per cent. yttrium oxide, and three-tenths per cent. cerium oxide, likewise increase the conductivity.

The report of the Allgemeine Elektrizitäts Gesellschaft to the stockholders states that the efficiency of the light seems to be about that of a small arc-lamp; that for convenience of handling it is superior to the arc-light but inferior to the incandescent lamp. Deri mixes the earthy oxides with difficultly fusible metal or graphite, both in the form of exceedingly fine powder. The tubes or filament made with the mixture are enclosed in vacuum bulbs or are surrounded with indifferent gas. The heat developed in the conducting material is communicated to the earthy oxide, causing it to glow and become conducting.

The production of nitrogen compounds, ammonia, and cyanides, which acquired such marked impetus a few years ago, seems to have fallen into the ordinarily recognized channels, and ammonia from coal and cyanides from animal refuse still control the markets. The extension of the by-product coke ovens has increased the ammonia production and will continue to do so, and we may expect that the immediate future will offer considerably enlarged supplies. The president of the Society of Chemical Industry offers the following statistics regarding the recovery of tar and ammonia in Great Britain :

	Tar. Tons.	Ammonium sulphate. Tons.
Gas works	650,000	130,000
Shale Oil Works.....	37,000
Blast-furnaces	150,000	18,000
Recovery ovens.....	62,000	11,000
	<hr/>	
	862,000	196,000
Possible production after extension of recovery ovens.....	620,000	110,000
	<hr/>	
	1,482,000	296,000

The by-product ovens are being everywhere extended. As already stated, the number of such ovens is rapidly increasing in this country, and we may expect that the tar and ammonia production resulting therefrom will have an important influence upon the market in these commodities. In Germany, likewise, where these ovens first secured really permanent foothold, the by-products have become important factors in the nitrogen supply market.

The utilization of atmospheric nitrogen is still attractive to investigators and inventors. The fixation of free nitrogen by the soil bacteria is now fully established, and the means for stimulating this important supply of available nitrogen have become the subject of most profound study and with gratifying results.

The fixation of atmospheric nitrogen by artificial, chemical, and mechanical means has likewise been the subject of encouraging study. Lord Rayleigh's results in the removal of nitrogen from the air by its oxidation through the influence of the spark or of the silent electric discharge, has directed study to the conditions and reactions involved and the possibilities of profitable fixation of nitrogen by such means. Shenstone and Evans find that under strong electric tension atmospheric oxygen suffers contraction and ozone is formed. Eighty to eighty-three per cent. of the oxygen may be so transformed, and under certain conditions ninety-eight per cent. But if the tension acts too long, nitrogen dioxide will be formed, the ozone will suddenly be destroyed, and the oxide decomposed. Vapor of water favors the formation of nitrogen oxide which, as Rayleigh found, must quickly be removed from the electric influence to avoid decomposition.

Crookes¹ discusses his suggestion that the nitrogen supply for agricultural purposes must be obtained by artificial means from the atmosphere, and bases some calculations regarding the possibilities upon the experiments of Rayleigh in oxidizing nitrogen to obtain a residue of argon, in which, with a consumption of one horse power he obtained chemical combination of 29.4 per cent. of a nitrogen-oxygen mixture. Hence one kilowatt hour would be required for seventy-four grams of sodium nitrate and 14,000 kilowatt hours for a ton (2204 lbs.). With steam power of the highest efficiency, the cost of which is placed at 0.67 cent per kilowatt hour, the cost is stated to be \$130. With water power costing 0.15 cent per kilowatt hour the cost would become \$25. Electrolytic niter should therefore compete with the natural product, but it is questioned whether the cheap power necessary to the production of the annually required 12,000,000 tons is available.

Moissan finds that nitrogen combines with calcium at dark red heat with incandescence. At 1200° C. the product obtained is crystallized, and its composition corresponds with N_2Ca_3 . In presence of alcohol this breaks up with formation of ammonia and calcium ethylate and with cold water it yields ammonia and calcium hydroxide.

¹ Crookes says: Nitrogen is a combustible gas, and the reason why, when once ignited, the flame does not continue to spread through the atmosphere and deluge the world in a sea of nitric acid, is that the igniting-point is higher than the temperature of its flame, not high enough, therefore, to set fire to the adjacent mixture. But by passing a strong induction current between terminals the air takes fire and continues to burn with powerful flame, producing nitric and nitrous acids.

Wolfram introduces calcium carbide into a bath of fused alkali hydrate. Carbon monoxide and hydrogen are liberated, the alkali metal is set free, issues in the form of vapor, and may be collected. If nitrogen or ammonia be passed through the fused mass cyanide will be formed.

Lance and Bourgrade and Emmanuel cause a mixture of nitrogen, hydrogen, and ammonia to act upon carbon heated from 1000° to 1100° C., whereby ammonium acetylide $(\text{NH}_4)_2\text{C}_2$ is formed, and this in turn combines with nitrogen to form cyanide. Ninety per cent. of the ammonia used is converted.

Vidal proposes generation of cyanide by heating phospham to 150° – 200° C. and allowing formic acid to flow into it. Hydrocyanic acid is said to be formed and volatilized to be collected in alkali. And Vittenet heats neutral copper acetate and ammonia of 21° B. in closed tubes two hours at 180° – 185° C. White opaque scales of copper cyanide are formed.

Conroy discusses Raschen's process for production of cyanides as practiced at Widnes, near Liverpool. The process consists in treatment of sulphocyanate with nitric acid, whereby sulphur is oxidized with production of sodium sulphate, hydrocyanic acid, and nitric oxide. The volatile and gaseous products are carried along, with vapor of water, into a tower filled with stones, where the water and part of the hydrocyanic acid condenses. The greater part of the hydrocyanic acid passes over and is condensed in water while the nitric oxide is subsequently converted into nitric acid.

A most important step forward in the production of ammonia has been developed by Mond, who found that nearly 100 pounds of ammonia could be recovered per ton of fuel from producer gases by introducing along with the superheated air required to burn the fuel in the producer, two and a half tons of steam for every ton of fuel consumed. The Solvay Process Company, at Syracuse, has erected a plant of eight Mond producers at their works, replacing the use of coal in the steam plant and elsewhere. The production of fuel gas with the recovery of ammonia is said to yield a return of twenty-five per cent. profit on the capital invested.

Waisbain, working under direction of Prof. A. Lidow, undertook dry distillation of wood by passing hot deoxidized gases through the material in the retort, obtaining in a small way much better results than are obtained by the old methods. He used generator gases, controlling their temperature, and found that at 150° C. the wood is not decomposed and only hygroscopic water is removed. Between 150° and 180° C. oxygen compounds, acids, and alcohol are produced. Between 280° and 350° gaseous hydrocarbons are formed, and finally, between 350°

and 430°. tarry products are carried over. In a small way the following results were obtained :

	Birch. Per cent.	Fir. Per cent.
Hygroscopic water.....	15.0	6.00
Pyroligneous acid (21.8 per cent. acetic)	10.9	6.45
Methyl alcohol	1.2	1.4
Charcoal.....	31.0	31.0

In a large way, because of defective condensation, less favorable results were secured, but the yield of charcoal of good quality for metallurgical purposes was 95.5 per cent. of the theoretical.

Bach applies practically the same system in a vertical furnace consisting of three parts. In the upper part he applies superheated steam, removing hygroscopic water, and in case of pine, turpentine. In the middle part the dried wood meets an ascending current of oxygen-free gases and vapors. A lower part, corresponding with the crucible of a blast-furnace, serves for partial combustion of the resulting charcoal to furnish carbon monoxide, thus providing the deoxidized gases to be used above and the heat necessary to the distillation. In the upper part of the furnace, which is of metal, the temperature is maintained at from 150°-300° C., and methyl alcohol and some acetic acid is formed. In the lower portion of the furnace, which is of masonry, more acetic acid and tarry products are formed. The products from each portion of the furnace may be withdrawn separately.

The very striking discovery of Buchner, that extract expressed from beer yeast has the power to convert sugar directly to alcohol, has been extensively discussed and the action has been ascribed to various causes, notably the existence of living germs in the extract and the presence of living protoplasm. The possibility of spores has, however, been removed by careful filtration of the extract, and Buchner has shown that living protoplasm is not possible, first by the action of poisons, and second, by first drying the yeast and making an extract with water, which is still active. Geret and Hahn find that the extract acts likewise upon albuminoids. The action is due to an enzyme, which may be precipitated by alcohol and separated from the solution with its activity unimpaired.

Sanguinati has made a study of the application of the molds to the fermentation industries and particularly of *Aspergillus orizae* of Koji, of *Mucor alternans* (Gayon) and *Amylomyces* (Roux) from Chinese beer yeast. All these have energetic saccharifying action. *Aspergillus orizae* first, then *Amylomyces*, and finally *Mucor alternans*. In distillery practice, however, *Amylomyces* is most useful, and because of its slightly

oxidizing action, is alone effective for use in the industry. This is the form used by Collette in Lille and in other French and Belgian distilleries. He proceeds as follows: He liquefies the starch without saccharification by heating the mass with addition of a small quantity of either acid, or malt, or pure culture of the mould or the diastase therefrom, or by pulverizing the starch paste mechanically. He then boils the mass in closed vessels to complete liquefaction and sterilization, then cools and aerates with pure air and inoculates with the mould spores. Saccharification and fermentation occurs and when the operation is complete the liquid is filtered from the residues. It is claimed that an increased yield of alcohol having a fine aroma and taste has been obtained.

Emmerling made experiments to determine whether, and in what proportion, formation of glycerine and succinic acid accompanies alcoholic fermentation of sugar solutions by mold spores. To start the fermentation he used *Mucor racemosus*, easily obtained pure from horse dung. In the fermented product he found both glycerine and succinic acid, the glycerine equivalent to eight and three-tenths per cent. and succinic acid to one and four-tenths per cent. of the alcohol. The fermentation with mold spores is therefore analogous to that of yeast spores.

Simonson has concluded his interesting experiments in manufacture of alcohol from wood sawdust. The process finally adopted consisted in conversion of the carbohydrates by boiling with acid, the ratio of liquid to sawdust being at least four to one and the acid content one-half per cent. The latter was neutralized before fermentation, which was effected at 25° C., and the best result was obtained with bottom yeast. The highest yield of alcohol reached seven and seven-tenths per cent. of the air-dried wood, containing twenty per cent. of moisture and corresponded generally with sixty per cent. of that required by theory for the total sugars present in the fermented liquids. The alcohol obtained was of excellent quality.

Goldschmidt makes sodium formate by heating sodium carbonate in a current of carbon monoxide under pressure. Then he heats together four parts of the crystallized sodium formate so obtained with five parts of anhydrous sodium carbonate in glass or iron vessels with exclusion of air to 400°-410° C., obtaining a mixture of sodium oxalate and formate. This obviates the losses incurred in heating the formate alone.

Zacher proposes manufacture of oxalic acid by first drying wood sawdust *in vacuo* to 100°-150° C. to remove twenty per cent. of the moisture ordinarily present. When dry, he slowly draws in upon the mass caustic potash solution containing six to seven per cent. of carbonate, the solution becoming heated to

122° C. Then the temperature is carefully increased while the mass is being stirred until 180° C. is reached. This is maintained three hours, when the bright-yellow mass is transferred to a hot plate provided with a stirring gear. Here the temperature is brought to 320° C. and so maintained four hours. The melt is a bright gray powder which makes an almost colorless solution. It contains no unchanged cellulose, contains about thirty-two per cent. of oxalic acid, and its solution yields with lime a nearly white precipitate of calcium oxalate. The best dry sawdust is preferable and the advantageous ratio of the sawdust to the caustic is one to two.

Eitner finds that in the extraction of tannin the yield suffers severely at temperatures above 100° C. Proctor and Parker found decomposition even at 100°. Eitner gives in the following table the most favorable temperatures for extraction of the different products :

Oak bark.....	80°-90°	Myrabolum.....	90°-100°
Mimosa bark.....	70°-80°	Sumac.....	50°-60°
Fir bark.....	90°-100°	Quebracho.....	80°-90°
Valonia.....	60°-70°	Divi-divi.....	50°-60°
Trillo-valonia.....	50°-60°	Canaigre.....	40°-50°

Whether for the industry or for analysis, he recommends that extraction be effected at lower temperatures, 40°-50° C.

The retting of flax has always been a troublesome problem and the process employed from time immemorial almost has been the subject of much thought and investigation. At last a more rapid and effective process seems to have been developed by Doumer and Swarte in France. It has been the subject of a favorable report by a commission appointed by the Ministry of Agriculture in France to investigate it. The flax is subjected in closed vessels, at carefully regulated temperatures, to the action of a liquid fertilized with *Amylobacter microbes*. When the action is complete the flax is drained, washed, and, without being disturbed, dried by a current of hot air. The product is reported to be superior to that obtained by retting in the open air.

The development of the cellulose products of Cross and Bevan is being pushed vigorously, particularly in England and Germany, under the names viscose and viscoïd. The former is obtained by combining alkali-cellulose with carbon disulphide, forming the sulphocarbonate and making a ten per cent. solution thereof with water. Viscose so obtained may be stored and transported in vessels of wood or zinc. Iron or copper vessels are attacked by it. It may be preserved in open vessels by keeping it covered with a layer of water, but it must not be subjected to temperatures above 20° C. At 10° it will keep two weeks. It changes, by decomposition, into an elastic mass of

hydrocellulose but passes through stages of gelatinous or half-solid forms. For the various uses its water content and the limits of age and decomposition must be carefully determined.

All its applications depend upon the recovery of the cellulose by its spontaneous decomposition. This is hastened when the product is spread in a thin layer, and it is caused partially by the liberation of carbon disulphide, although part of the change is much more profound. The decomposition may be governed by regulation of the temperature. A film produced on glass, heated to 100° C., becomes entirely insoluble in water.

Viscose, allowed to decompose in large blocks, forms a transparent mass insoluble in water and known as *viscoid*. To insure a perfectly homogeneous product, decomposition must proceed without intervention of heat.

It has been usefully applied to the sizing of paper and tissues adding greatly to their strength. To this end the viscose, after application, must be decomposed promptly, and in the works this is effected by means of sulphur dioxide or metallic salts. The latter form insoluble sulphocarbonates, and that of zinc has been found the most effective. Goods sized with it become water-proof, and if the sizing be sufficiently thick, the finished product has the appearance of leather. It makes fine photographic films, and when spun has the appearance of silk. A wide field of usefulness is predicted for it.

The new product of the laboratories of Cross and Bevan bids fair to find many useful applications. It is cellulose tetracetate and is formed by the reaction taking place between cellulose, magnesium acetate, and acetyl chloride, as indicated in the following formula :



In manufacturing, this reaction can be carried out quantitatively. By a similar reaction the butyrate may be formed. These products are difficultly inflammable and behave with solvents like the nitrate, giving solutions of a colloidal nature. Their solubility differs from that of the nitrate. The acetate is completely insoluble in methyl alcohol, ethyl alcohol, amyl acetate, acetone, and ether, but soluble in ethyl benzoate, chloroform, epichlorhydrin, aceticanhydride, glacial acetic acid, and nitrobenzene. The solution of the tetracetate in nitrobenzene hardens, on cooling, into a solid but completely transparent jelly. The solution in chloroform, epichlorhydrin, or ethyl benzoate may be diluted to any degree with acetone without causing precipitation. Spread upon glass plates, it gives beautifully transparent films, which are continuous if their thickness is within that of iridescent films.

The tetracetate is indifferent to chemical reagents and as resistant to all acids, except nitric, as the nitrate. Aqueous alkalis, which even in the cold break up the nitrate, do not attack the tetracetate even at high temperatures. Alcoholic soda solution saponifies but does not disintegrate very thin sheets or destroy their transparency. Its insulating power is as great as that of gutta percha or rubber, and it withstands temperatures up to 150° C. In its resistance to chemical agents and its electric properties, the butyrate is similar to the acetate, but it is more soluble than the acetate and dissolves in ethyl acetate and acetone.

Weber, from whose interesting paper the facts quoted are taken, declares that these products will take the place of the nitrate in many respects, and they are particularly valuable because of their resistance to chemical agents, heat and electricity, and their non-inflammability. They are recommended for metal lac.

Fraenkel and Friedlaender find that when cotton yarn is mercerized with alcoholic alkali the strength of the product is greater than when aqueous alkali is used. Mercerization occurs only after immersion and removal from the bath. They found that yarn having a strength of 358 grams supported 553 grams after mercerization with aqueous lye of 35° B., and 618 grams when treated with cold alcoholic alkali and 720 grams with warm alcoholic lye.

Effort, directed to the production of artificial silk, continues in spite of the discouragement offered by the very low prices of the natural product. The cellulose products have thus far been the most promising and Chardonnet's process is carried on commercially. In this process cellulose is nitrated until it appears bright blue in polarized light, carefully washed and dissolved in the alcohol-ether mixture. After filtration it is spun through fine apertures, dried in chambers heated to 45° C., denitrated by alkaline sulphides, bleached, and finally, if desired, dyed with basic colors. Pauly, of Basle, dissolves carefully cleansed cotton in ammoniacal copper oxide solution, and passes the solution through fine apertures to rollers revolving in acetic acid. The fiber is washed and dried in warm air.

Stern dissolves cellulose in strong alkali and carbon disulphide, makes up to ten per cent. solution with water and forces the viscous solution through fine jets into ammonium chloride solution. It is wound on reels from this solution, washed with hot sodium carbonate solution, bleached, washed thoroughly, and dried under tension in air or a heated chamber.

Millar subjects filaments of gelatine to vapor of formaldehyde. The product is insoluble in water, takes color well, but has neither the strength nor the brilliancy of the natural product.

These are some of the advances the year has brought forth. The prevailing demand for material of every description in the arts is encouraging and must stimulate further progress, and we may reasonably believe that the near future will be fruitful in new discoveries.

WM. McMURTRIE.

NOTES.

*Chemical Detection of Vegetable Fibers.*¹—This process rests on the property which cellulose possesses of transforming itself under the action of sulphuric acid into carbohydrates, possessing an aldehydic function, which can easily be detected by the colored reaction it gives with the phenols.

The sample to be examined—suppose it to be a piece of woolen goods in which the cotton is to be detected—is, after careful washing, treated by sulphuric acid at 20° B. and heated one-half hour over the water-bath. The imperfect solution is then diluted and the carbohydrates looked for in the following way: In a test-tube about one centigram of a phenol—say resorcine—is introduced, one or two cc. of the preceding solution added, and concentrated sulphuric acid perfectly free of nitrous products poured along the side of the tube, so as not to mix it with the solution therein. The heat evolved is generally sufficient to develop a coloration at the plane of separation, and the intensity of this color can be increased if necessary by gentle heating in the water-bath. If this product resulting from the treatment of cotton is brought up to 1 part in 1000, the resorcine will give an orange, the alpha-naphthol a purple, the gallic acid a green, becoming gradually violet down in the acid, the hydroquinone and the pyrogallol a brown, the morphine and codeine a nice lavender, the thymol and menthol a pink color, etc.

The extreme sensitiveness of these reactions allows us to characterize cotton, even in dyed goods, using bone-black to decolorize the solution if absolutely necessary. An approximation as to the quantity of cellulose can be obtained by comparing the intensity of the coloration to the one given by a solution of cotton of a known strength.

As we have lately indicated, the oxycellulose, owing to its aldehydic function, gives, too, with the phenols, colored reac-

¹ Read before the Rhode Island Section, June 15, 1899.