REVIEW.

SOME RECORDS OF THE YEAR'S PROGRESS IN APPLIED CHEMISTRY.[1]

To present in a single paper even a limited review of what the year has brought forth in the application of chemistry in the arts and manufactures is a difficult task. So manifold have been the discoveries of new facts and the new applications of old ones that to cover all that has been accomplished in the several fields would be beyond the capacity of any individual or of the space or time that could be devoted to a single paper. In the present instance, therefore, it will be possible to present only such as have specially interested the writer and seem to be of interest and value to those to whom this paper may come.

It was said of old "it is not well for man to be alone," and this applies to chemists as well as to those interested in other departments of human activity. Personal exchange of thought and experience is the best stimulus to further endeavor, and so the various meetings and Congresses do their share in the promotion of the interests which most nearly concern us. Of these, several have been held in various localities with most gratifying results. The Third Congress of Applied Chemistry was held in Vienna in the closing weeks of July and was well attended, while the work done was of the highest character. 765 members were in attendance. The Congress was divided into fifteen sections and subsections which held seventy-six separate meetings and discussed, in all, 171 subjects. At the closing session it was proposed and determined that the next meeting should be held in Paris, in 1900. The proceedings of the Congress will be published promptly and will constitute a valuable record of the more important advances made during the year.

Likewise the annual general meetings of the Society of Chemical Industry of England and of the Vereins Deutscher Chemiker of Germany, have been held and the work of these organizations, respectively, will be published in their own Journals.

Chemical industries are perhaps more flourishing and more widely extended in Germany than in other countries though they are becoming far more numerous from year to year everywhere. Doubtless the figures of Wenzel regarding Germany may be accepted as, in a measure at least, reflecting the conditions prevailing throughout all the countries in which such industries flourish. Thus he states that at the close of 1896, in Germany, 96 chemical works with 256,038,900 marks capital gave a total return of 31,495,900 marks in dividends, or an average of 12.3 per cent. against 8.9 for 1897. In these figures the tar

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[1] Read before the New York Section of the American Chemical Society, Oct. 7, 1898.

industries gave the highest, nearly 24 per cent., and the fertilizer industries the lowest net returns. The general commercial and financial depression of the past years seem, therefore, to have influenced the chemical industries as well as many others.

In the metallurgical processes but little progress seems to have been made. In the extraction of gold and silver by chemical means the chlorination, bromine, and cyanide processes still hold favored places and they seem to have reached positions having little room for improvement. Most interesting, therefore, is the announcement that Dupre has been able to extract gold with an inexpensive solution containing sodium thiosulphate and ferric halides (chloride, bromide, or iodide) together with an acetate. The mixture of these substances together in water yields a dark red solution capable of dissolving gold and its compounds from sulphide and other ores without attacking the base sulphides. It is stated that a solution containing two per cent. sodium thiosulphate, 0.75 per cent. ferric chloride, and one to two per cent. calcium acetate and diluted to two, three, or even ten times its volume with water, will serve for the extraction of the most varied kinds of gold ore, and that for equal volume and equally exposed gold surface this solution will dissolve, in six to twelve hours, fifteen to twenty times as much gold as a one to two per cent. cyanide solution in equal time. The gold probably passes into solution as sodium gold thiosulphate which may be decomposed for recovery of the gold by zinc, by electrolysis or by the action of sodium nitrate and sulphuric acid. The process seems to be worthy of careful consideration.

The extraction of zinc, particularly when associated with other metals, has always been troublesome and costly and generally impracticable. In this direction more progress has probably been made than in any line of metallurgical work, and several successful methods for the economical and commercial separation of zinc from other metals have been devised during the past year or two. Ashcroft carefully roasts the ore and extracts the roast with sulphuric acid alone or in admixture with ferrous sulphate. The iron salt is decomposed by the zinc oxide, the zinc sulphate passing into solution ; the solution obtained by filtration and washing the residue is concentrated until it contains 250 grams of zinc per liter and electrolyzed to removal of 75 per cent. of the dissolved metal. The solution is used on a new lot of ore, or the metal is recovered from it by precipitation. The lead residue is smelted for argentiferous lead.

Siemens likewise roasts the ore carefully, converts the gases into vitriol, extracts the roasted ore with the vitriol produced, electrolyzes the solution to separate the zinc and smelts the residues for argentiferous lead.

Hall leaches the carefully roasted ore with vitriol but he decomposes the solution with magnesium carbonate, obtaining zinc carbonate which, by heating, he converts into zinc oxide.

Fry, David, and Ledoux, melt the carefully roasted ore with one-fourth its weight of sodium sulphate or bisulphate, and one-eighth its weight of iron oxide in a cupola furnace. It is stated that in the smelting process ninety per cent. of the lead is obtained as metal carrying all the gold and silver, the zinc passing into the fusible slag. The latter is heated with carbon in a Siemen's furnace, the reduced and volatilized zinc burned to oxide, which is collected in dust chambers, resulting in a recovery of eighty per cent. of the zinc. The process is applied in Swansea each week to 400 tons of ore containing twenty to thirty-five per cent. lead, twenty-five to thirty per cent. zinc, thirty ounces silver, and a little gold.

Frank in Berlin extracts zinc electrolytically in a mixed process. He uses a three-cell bath. The anode space contains alkali chloride; the cathode space an alkaline zinc solution and through the intermediate space separated from the others by diaphragms, alkali chloride solution is made to circulate. Zinc is collected at the cathode, chlorine at the anode, and the intermediate space is said to contain chloride and free alkali, the latter to be separated, and recovered by evaporation.

The electrolytic process of Hoepfner is applied to refining of zinc in England, with success and profit. It is stated that one E. P. yields one pound pure zinc, while refining of an equal weight of copper requires only half as much energy.

Tommasi proposes to replace other processes for desilverization of lead by electrolysis obtaining, at the same time, lead of the highest degree of purity. The electrolyte consists of a solution of acetates of sodium and lead. He uses a current of 6.75 volts and 1800 ampères for each bath, and reduces internal resistance by bringing the electrodes closely together. The metal dissolves from the anode, and is deposited on the cathode, whence it is carefully scraped off as cement lead which is fused with carbon, while the silver is deposited as slime. The inventor claims that lead containing 150 to 200 grams of silver per ton, can be profitably worked at a cost of ten francs per ton.

In the extraction of nickel, Mond seems to have made some further progress in the application of the carbonyl reaction. It will be remembered that he first reduces the oxide, and for the more effective action in the subsequent step, this should be done at a temperature not above 350° C.; that he next subjects the reduced metal to the action of carbon monoxide at a temperature of 50° to 60° C. which is most suitable for the reaction producing the carbonyl compound; he then subjects the latter compound to a higher temperature for its decomposition.

He has elaborated an apparatus for practically continuous operation consisting of a "reducer" and a "volatilizer," but both these may be combined in the same apparatus. In a vertical cylinder are arranged alternately a series of plates and hollow boxes, one above the other. The boxes have the same diameter as the cylinder, and the plates are slightly smaller leaving an annular space at their peripheries. Each box has an opening at the center. A vertical shaft through the center with properly constructed stirring arms forces the material to be treated from the center of the plate to the periphery over which it falls to the surface of the box, and is drawn to its center when it falls to the next lower plate and so on in succession. The boxes are arranged to receive and discharge, at the will of the operator, steam, hot air, or cold water. The boxes of the upper part of the apparatus heat the ore to the reducing point, the boxes at the lower part cool it to the volatilizing point. When properly cooled it is sent to the volatilizer, and the treatment completed. The method seems likely to have practical application.

Storer extracts the metal from New Caledonian ores by heating the finely pulverized ore with ferric chloride solution in a closed vessel to a temperature of 190° C., five to eight hours. A solution of nickel chloride containing a little ferric chloride is obtained, and the latter is subsequently removed by lime.

Coehn bases a method for separation of cobalt and nickel upon the fact that in the electrolysis of the solutions containing them the former will separate as peroxide at the anode while the latter will not. Even in the presence of large quantities of nickel the cobalt deposit is free from it. To prevent the deposition of nickel at the cathode, a more easily separable metal such as copper (in form of sulphate) is added to the solution. It is believed that the reaction will find application both in the laboratory and in the works.

Lebeau produces beryllium (glucinum) by electrolysis of its double fluoride of sodium or potassium, using a cathode of nickel and an anode of carbon, and operates at a temperature corresponding with red heat with a current of eighty volts and twenty ampères. The metal obtained contained 99.5 to 99.8 per cent. beryllium, and had a specific gravity of 1.73. It does not oxidize in dry air but burns brilliantly in oxygen. Halogens attack it, and dilute acids dissolve it. It combines at high temperatures with nitrogen, boron, silicon, and carbon, and forms carbides, which with water yield the hydrate and methane. It forms alloys with other metals, those with copper being malleable, and capable of taking high polish which does not readily tarnish in the air.

Goldschmidt and Vautin made use of the very high heat of combustion of aluminum, which is 360,000 calories, for the production of high temperatures, and the reduction of the very refractory metallic oxides, and by means of it has been able to separate chromium, titanium, manganese, iron, copper, etc. To effect this it is only necessary to intimately mix the finely pulverized oxide with very finely divided aluminum and start the combustion. It proceeds quickly to a finish, producing temperatures up to 3,000° C. and reducing the metals free from carbon.

Franck has likewise utilized the high combustion temperature of aluminum for the reduction of oxides both metallic and nonmetallic and particularly for the production of phosphorus. For this latter purpose he mixes the metaphosphate with silica and aluminum, and heats the mixture to start the combustion when the reduction proceeds quietly; the phosphorus distils readily and yields an excellent product particularly when the lime compound is employed.

Various other methods for production of phosphorus have been devised in which the electric furnace is employed to attain the high temperature requisite to proper reduction. Thus Hilbert and Franck and Gin and Leleux, working independently, heat properly proportioned mixtures of phosphatic material and carbon in the electric furnace, the ensuing reaction producing calcium carbide and phosphorus. The phosphorus volatilizes and is collected. Collardeau makes calcium phosphide in the electric furnace, generates hydrogen phosphide with it, and decomposes the gas by passing it through a strongly heated coke-lined tube, and collects the phosphorus liberated; and Boubleque decomposes electrolytically the iron phosphide obtained by fusing together iron compounds and calcium phosphate, and removes the liberated phosphorus by a current of indifferent gas. In Germany the price of phosphorus has further declined and reductions of 0.40 M. for white and 0.80 M. for red are quoted. The production has increased in France, as well as in Russia, is extending to Germany where several works have been projected and the English monopoly is seriously threatened. Likewise at Niagara Falls, and elsewhere in this country, electrolytic processes have been applied and further fall of price may be expected.

Ronco has discussed the various electrolytic methods for production of white lead. From him we learn that Turner Bottome electrolyzes an alkaline salt solution containing sodium or potassium carbonate, between lead electrodes, passing a current of carbon dioxide through the solution during electrolysis. White lead is said to precipitate leaving the electrolyte unchanged. Ferranti and Noad use ammonium acetate as the electrolyte with lead electrodes separated by a diaphragm. After proper time the anode and cathode liquors are mixed together and carbon dioxide passed through the mixture, and Luckow uses a solution containing one and five-tenths to two per cent. of a mixture of salts consisting of eighty parts of a salt whose acid makes a soluble salt with lead and twenty parts of alkali carbonate. He applies to this solution a current of five-tenths ampère per sq. dm. and two volts between anodes of soft lead and cathodes of hard lead while passing carbon dioxide through the electrolyte.

Progress in the alkali industry has been confined to the electrolytic processes so far as can be learned from the literature. We are told that in England the production of alkali by the Leblanc process has considerably declined while that by the Castner electrolytic process has increased, and the Hargreaves and Bird process gives promise of extension during the present year. The Kellner-Partington Paper Pulp Company at Sharpsborg, in Norway, have projected a large electric plant to utilize the water power of the place. In addition to this a new company, the "Hafslund Aktieskab", has been organized and will erect, on the other side of the falls, an electric plant of 25,000 horse-power, the latter to supply power for works, and for electrochemical works, particularly the manufacture of aluminum and carbide. The status of the utilization of power for generating electric energy for use in the alkali and bleach industries in Europe is illustrated in the following table :

Golling—water-power	3000	H. P.	in construction.
Solvay, Bernberg	1000	"	in operation.
Solvay, Belgium	2000	"	in construction.
Solvay, Russia	4000	"	projected.
Castner-Kellner, Runcorn, England	1000	"	in operation.
Castner-Kellner, Runcorn, England	4000	"	projected and in construction.
Chemische Fabrik, Gresheim, Bitterfeld	4000	"	in operation.
Algemeine Electricitäts, Gesellschaft, Bitterfeld	3000	"	in construction.
Electro-Chemical Co., St. Helens, England	1100	"	in operation.

Kellner of Halle, discussing the status of the electrolytic alkali industry in the International Congress of Applied Chemistry in Vienna, states that three processes are now used : (1) Electrolysis of alkali chloride with the aid of diaphragms ; (2) electrolysis of a fused electrolyte ; and (3) electrolysis of alkali chlorides with the aid of the mercury cathode.

The diaphragms which have given the best results. he says, consist of, first, salt, and second, soap or cement, all having the disadvantage that they need a low tension current, and large apparatus compared with the yield, low concentration of the alkali solution, and finally contamination of the latter with undecomposed electrolytes. He considers that electrolysis of the fused electrolyte leaves much to be desired.

The mercury diaphragm is most used, and has been variously applied by Sindig-Larsen, Castner, Strömers, Rhodin, and others. He denies any objection to their use from a sanitary standpoint, but states that flouring of the quicksilver must be avoided because of the tendency to formation of mercuric chloride with corresponding loss of mercury.

The Hargreaves and Bird process seems to be responding to the persistent work done with it, and shows promise of successful extension and development. Carbon anodes, and iron gauze cathodes are used and between them is arranged a diaphragm of secret constitution and construction. Steam washes the soda from the cathode, and chlorine from the anode is carried to a lime-box. Dr. R. Lucion, of Brussels, reported to the International Congress of Applied Chemistry, that his observations led him to consider that the probabilities of the ultimate successful operation of the process are slight. The diaphragm, he says, apparently consists of an iron screen upon which pulped asbestos has been floated, exhausted by suction and then saturated with a siliceous solution, and the general construction of the apparatus admits of the use of very impure solutions. The capacity of the apparatus referred to by Lucion is elsewhere stated to be : for each cell with ten square meters of diaphragm and cathode surface, decomposition of 106 kilos of salt producing, in twenty-four hours, 117 kilos of bleach of thirty-seven per cent. available chlorine, and 280 kilos crystal or 95 kilos calcined soda. This cell uses a current of 3.9 volts and 2300 ampères equivalent to 14½ E. P., costing $1.75 daily. The soda contained 97.7 per cent. sodium carbonate and one per cent. sodium chloride. Plans for enlarged construction have been projected but operations have thus far been carried on, apparently, only on a small scale.

Blount discusses the relative possibilities, cost, etc., of the Leblanc soda process and the electrolytic processes, and he finds that while the Leblanc process requires five and three-tenths tons of coal for one ton of caustic and by-products, the electrolytic process consumes but from three and two-tenths to four and two-tenths tons. He considers that although comparison of the two processes is very difficult it may be stated that the electrolytic processes are direct, clean, requiring inexpensive hand labor, and yielding no troublesome by-products, but on the other hand the apparatus required is extensive and costly and rapidly deteriorates.

The chemical processes give large yield with few pieces of apparatus but very large and inexpensive ones, requiring but little repair. Much hand labor is required, and an enormous quantity of worthless and troublesome waste-products result.

In the production of chlorates the electrolytic processes seem to have taken the lead. Spilker and Lowe using a specially constructed apparatus electrolyze solutions of potassium chloride which in the anode cell is saturated with lime. The saturation of the anode liquid with lime, is maintained in the circulation which constitutes part of the process and the temperature is kept at 40° C when only chlorate is formed. Oettel likewise found that better yields may be obtained with a given current in producing calcium chlorate than is possible with potassium chlorate. Bischoff and Forster find the cause of this to be the lower solubility of the calcium hydroxide produced at the cathode and covering the latter with a thin layer thus minimizing its reducing influence. For best results they recommend a ten per cent. solution of calcium chloride, a current of ten ampères per square meter at the anode, and twice this strength at the cathode because of the calcium hydroxide formed on the latter. If the solution be heated to 50° C. the current tension is found to be the same as for potassium chloride.

Vaubel suggests addition of alkali bicarbonate to the anode liquid when alkali chlorides are being electrolyzed for he finds that in presence of the acid carbonates conversion of chloride to chlorate in the anode cell is complete. While the laboratory experiments gave satisfactory results, they were not confirmed by work on a larger scale.

The number of bleaching agents available in these latter years has been largely increased but much work remains to be done to perfect many of them. The old "bleach" (chloride of lime) still holds its place, yet the new bleaching processes are pushing it very hard. Thus the experiments of Cross and Bevan and of Clayton and Beadle show that bleaching with the Hermite solution consumes less chlorine for a given weight of fiber bleached while the time required for effective operation is enormously reduced. The relative efficiency of the Hermite solution and the chloride solution is as five to three. It was further found that the bleaching solution is more effective when kept in motion and that movement effects a saving of from thirty-seven to forty per cent.

The possibilities of the use of oxygen in its condensed forms seem to be growing with the development of improvements in the generation of electricity. Manufacture of sodium peroxide commercially is extending and the persulphates and percarbonates are attracting deserved attention. The process of Castner or some modification of it seems to be that almost exclusively used in the manufacture of sodium peroxide. The material is used in slightly alkaline solution, excess of alkali being controlled either by magnesium sulphate which is effective or by oil of vitriol.

Little has been added to the work of Marshall and Hansen in the production of the persulphates and percarbonates. Low temperatures seem to be absolutely essential to their formation and that of persulphuric acid is likewise favored by the addition of small quantities of hydrochloric acid. Practical utilization of these products has not yet been reported. The use of ozone in bleaching is being applied by Siemens and Halske to the treatment of linen and yarns and of starch and its products, and they are devoting special attention to its production.

The production of chlorine by electrolysis is rapidly extending and must eventually, it would seem, replace other processes. The apparatus and methods of Castner and Kellner have found most favor but other and numerous ones have been devised. Yet as already stated practically all leave much to be desired. Hunt and Watson use ferric chloride in the cathode cell with an iron cathode, and potassium chloride in the anode cell and use the chlorine liberated for production of hypochlorite. Haber, on the other hand, electrolyzes strong hydrochloric acid directly and obtains a yield of 100 per cent. If the acid be dilute, hypochlorous acid is formed and with very weak acid oxygen is liberated.

Hammerschmidt and Hess have lately discussed in the *Chemiker Zeitung* the electrolytic production of oxygen, setting forth its advantages and a review of their statements will be of interest. They state that the gas produced by the Brin process contains only ninety per cent. and that obtained by the Linde liquefaction process only seventy-five per cent. of oxygen, and that either method consumes from one to three horse-power hours for the production of one cubic meter of gas.

A perfect electrolytic method remains to be devised, but of those which have thus far been brought forth by d'Arsenoval, Latchinoff, Renard, Dehnard, Siemens Brothers, Garuti and Schuckart & Co., the authors particularly commend that of the last named. The cells employed are of iron and hard rubber, the current used in practice 300 ampères and three and two-tenths to three and three-tenths volts, the temperature of the electrolyte which is a caustic soda solution, 60°C. With these conditions they have determined that sixty kilowatts or ninety horse-power will produce in twenty-four hours 100 cubic meters of oxygen and 200 cubic meters of hydrogen. This involves a plant costing something over $20,000 and a daily operating expense of between $30.00 and $35.00. Garuti's process yields *knall* gas at 4.15 pf. per cubic meter and oxygen at 12.5 pf. per cubic meter. If steam-power is used, twenty-one and sixty-two pf. respectively. Latchinoff likewise electrolyzes a sodium hydroxide solution of ten to fifteen per cent. in an iron vessel using a sheet iron anode enclosed in parchment paper stretched over an ebonite frame. The current tension is two and five-tenths volts and the cost of producing two cubic meters of hydrogen and one cubic meter of oxygen is estimated at about sixty-five cents. The gases are of a high degree of purity and the processes therefore promise well for the future.

Kassner passes air over warmed calcium plumbate until oxidation is complete, removes residual nitrogen by steam, follows this with a current of carbon dioxide liberating the absorbed oxygen, purifies the latter by well-known means and claims to secure a product testing ninety-nine per cent. Lapointe heats a mixture of caustic soda and manganese dioxide in a current of air, exhausts the gas remaining at the close of the oxidation period, decomposes the manganate with superheated steam, and claims to obtain oxygen free from nitrogen.

Shenstone and Evans discussed, before the London Chemical Society, the influence of electrical tension upon atmospheric air. Under such influence air rapidly contracts, then quickly expands again, containing a trace of nitrogen tetroxide. In the presence of moisture eighty to eighty-five per cent. of atmospheric oxygen may be converted into ozone and with care the conversion may be carried to ninety-eight per cent. If not carried too far no nitrogen tetroxide is formed but there arrives a point at which this occurs. This compound favors the destruction of the ozone by the electric tension. The presence of moisture favors the production of ozone and hinders that of nitrogen tetroxide.

To reduce the temperature of the air and so favor the generation of ozone Andreoli constructs an apparatus with cooled electrodes, the latter consisting of rectangular boxes, each provided with inlet and outlet for cooling liquid and provided with its own circulatory system. Its surface is covered with pointed projections like saw-teeth. The air passes in at the bottom, and out at the top of the chamber in which these electrodes are enclosed.

The same principle influenced Otto in the construction of his apparatus for polymerization of gases and particularly oxygen by the electric spark or a current of high tension. To this end he frequently intermits the current and so prevents heating the apparatus. In one form he arranges two sets of electrodes one of which is fixed, the other parallel with the first and set in sectors of a movable disk. The two sets being properly enclosed and each connected respectively with the poles of a conductor carrying a current of about 18,000 volts, the disk is rapidly rotated causing its set of electrodes to successively pass those of the fixed part. With the current of the tension stated the electrodes should be about three centimeters apart. When the apparatus is in motion and the current is passing, rapid sparking ensues. If air or oxygen be passed between the active surfaces ozone is rapidly produced. In another form of apparatus two concentric cylinders are arranged, one with the electrodes in rings, the other or inner one with the electrodes set spirally about it. The inner cylinder is made to revolve, and its electrodes rapidly pass in succession those of the outer cylinder. When the current is operating and air or oxygen is passed through the annular space, ozone is rapidly produced. Claim is made: (1) for the use of electrodes arranged, and used as described for effecting polymerization, combination or decomposition of gases, and (2) for producing ozone and other substances; for instance, cyanogen from nitrogen and acetylene, nitrated products from nitrogen and oxygen, ammonia from nitrogen and hydrogen. A similar form of apparatus is said to have been devised for utilization of Lord Rayleigh's plan for obtaining oxidized products from the atmosphere.

We may not leave the discussion of the forms of oxygen without some mention of liquid air which certainly gives some promise of application in an industrial way. It is interesting to note that the process for liquefaction of air depending upon the rapid cooling of the compressed gas by the expansion of a portion from a higher to a much lower pressure should have been brought out almost simultaneously by three different persons in as many countries. Linde in Germany, Hampson in England, and Tripler in this country seem to have attained the same end by the same means at about the same time. The process of Linde which does not differ essentially from that of the others named consists of an air-compressor and a return current apparatus. The air is first compressed to sixteen atmospheres, then to 200 atmospheres, and the water removed from it. Then it is passed through a coil enclosed within a second, the tubes of each coil being concentric. From the inner coil the air compressed to 200 atmospheres is allowed to expand into the annular space between it and the outer coil to sixteen atmospheres, and return to the compressor where it is again compressed to 200. A second compression and expansion reduces the temperature to the critical point and the air is liquefied. The entire apparatus is naturally protected by a non-conducting covering.

The liquid air so obtained contains thirty-seven per cent. oxygen and sixty-three per cent. nitrogen because of the more ready volatilization of nitrogen.

With a Linde machine it is possible to produce a mixture containing equal volumes of oxygen and nitrogen with a consumption of one horse-power for each cubic meter. It has been stated that the European practice yields about three-tenths liter per horse-power which is somewhat better than, so far as we can learn, has been attained in this country. There is no doubt, however, that with better apparatus, and the most economical power generation, much better results are possible.

With the low temperatures available through the rapid evaporation of the liquid air, new fields of interesting investigation of the physical properties of bodies and of chemical reactions, are made possible. Whether the oxygen-enriched mixture can be produced at sufficiently low cost and will be effective enough to be applied to such industrial reactions as the oxidation of hydrochloric acid in the production of chlorine or the oxidation of sulphur dioxide in the production of sulphuric acid as has been suggested, remains to be established ; but with proper arrangements for compression and for preservation of the liquid there seems to be no reason why it should not replace other agents, such as ammonia, sulphur dioxide, carbon dioxide, etc., in refrigeration.

In the production and utilization of calcium carbide, some progress seems to have been made; at any rate our knowledge regarding them has been considerably widened. Dr. Sieber discusses the heat requirements and finds a wide difference between those of theory and practice and justifies the efforts being made to improve manufacturing conditions with this regard. He estimates that one E. H. P. should yield 9.38 kilos of carbide in 24 hours, but in practice only four to five kilos are obtained showing that a large portion of the energy employed is consumed in heating the reacting mass. Again practice requires one and three-tenths kilos of carbon and one and four-tenths kilos of lime while theory requires six-tenths and nine-tenths kilos respectively, for one kilo of carbide. The power consumed, therefore, becomes 3230 watt-hours for heating and 1900 watt-hours for reaction. One E. H. P. should, therefore, yield in twenty-four hours 3.44 kilos. Since in the generation of electrical energy scarcely more than fifteen per cent. of the fuel energy is realized, it is plain that economy requires that the materials used should be heated before they enter the furnace and are subject to the action of the current. He suggests the use of the carbon monoxide generated for this purpose. If water-power is available, of course this is of less importance. Pictet likewise realized the importance of this, and has devised a specially constructed furnace having it in view. Into his furnace he charges coke and lime, the former being in considerable excess over that required for the final reaction. Into the upper of three zones he injects air, and by the resulting combustion of the excess of carbon a temperature of 2,000° C. is attained. Into the next lower zone he injects oxy-hydrogen gas, the combustion of which produces a temperature of 2,300° to 2,400° C. In the bottom zone are arranged electrodes with the arc immediately over an outlet. The carbide formed flows out through the opening and is collected underneath. Practical results of use of the furnace have not been given.

Hausermann recommends casting the carbon and lime into blocks or sticks before charging to the furnace, the principal object being to avoid production of partially converted dust which thus far has found no valuable application.

Regarding the cost of calcium carbide Desiré Korda states that one horse-power day should produce four kilos of carbide which would bring the cost to about $50 per ton.

The Neuhausen Company quotes the product at 300 francs, say $60 a ton. The author considers that the cost claimed by certain American producers is too low but the exports of the product from this country would not seem to confirm this.

It is now generally accepted by the best authorities that much of the danger and loss incident to the manufacture and use of acetylene is to be ascribed to the high temperatures produced in the generators employed. Gerdes reports that determinations of heat generated in the decomposition of calcium carbide shows it to amount to 1,200 calories for each kilogram of gas liberated. Lewes, operating with an apparatus of his own device, concludes that 406 calories fairly represent the heat of decomposition of one kilo of commercial carbide and he estimates that for pure carbide the figure should be 444.6. This varies somewhat from that given by Gerdes but the observers doubtless had different qualities of carbide. At any rate it is evident from the figures given that the temperature in the generators may readily reach the danger point. Pure acetylene suffers decomposition at 780° and Gerdes states that when mixed with a certain quantity of air this may even occur at 480°. Lewes, in a large series of experiments, found the temperatures in generators, in which a comparatively small quantity of water took part in the reaction, rose to from 703° to 807° in different cases. Under such circumstances, deBrevans states that polymerization occurs with the production of liquid hydrocarbons such as benzene, styrolene, etc., reducing the illuminating power. Acetylene produced by Lewes in his experiments and analyzed by him contained :

	I.	II.
Acetylene	70	69.7
Saturated hydrocarbons	11.3	11.4
Hydrogen	18.7	18.9

He states that this change reduced the illuminating power from 240 candles to about 126. Benzene is the principal product of the decomposition and is the most conducive to difficulties, such as stoppage of pipes by its condensation, of the burners by its decomposition, giving tarry products and giving smoky flames. Both Gerdes and Lewes recommend the use of large volumes of water in the generator, allowing the carbide to fall into the water ; both recommend that the temperature shall not rise above 100° in the generator. Pictet even recommends that the water used shall be cooled at 10° C. and be maintained at this temperature within the generator by special arrangement to that end. Bamberger likewise recommends using large quantities of water into which the carbide may fall in order to reduce the generation of ammonia from the nitrides and cyanides.

The poisonous qualities of commercial acetylene are believed to be due to the phosphorus and sulphur compounds it contains when recently generated. So likewise the dangerous character of the gas and its explosiveness are believed to be due to the presence of these compounds. This latter view is not sustained by the results of the experiments of Lewes which showed that in order that the gas may become spontaneously inflammable from such admixture it must contain over eighty per cent. of hydrogen phosphide. Lewes observed however that cases of spontaneous ignition occurred in the generation of gas when the carbide used contained even as low as one per cent. of calcium phosphide. Yet in spite of this fact, he expressed the opinion that ordinary commercial carbide could be used without danger from this cause.

Hubou finds the impurities of calcium carbide to be lime and coke, carborundum, silicides, nitrides, phosphides, arsenides, and sulphides. Lewes found the same impurities. It is natural therefore that the gaseous products of decomposition of these substances by water should be found in acetylene. So Girard found that gases containing 95.9 to 99.5 per cent. of acetylene, four-tenths to two and nine-tenths per cent. of nitrogen, 0.08 to 1.19 per cent. of carbon monoxide, and no oxygen, contained likewise per cubic meter two and seven-tenths grams of ammonia, 0.44 to 1.78 grams of hydrogen phosphide, 0 to 13.42 grams of hydrogen sulphide. Lewes found an average of 0.65 per cent. of hydrogen phosphide between limits of 0.02 and 2.30 per cent. DeBrevans found hydrogen phosphide, silicide, and sulphide, ammonia, ammonium sulphide, sulphur dioxide, cyanogen and sulphocyanogen compounds, and these results have been confirmed by Vertess, Bamberger, and others. Bamberger ascribes the presence of ammonia and cyanogen compounds to the nitrides and even cyanides formed in the furnace. Nitrides of aluminum and magnesium decompose in presence of water, forming ammonia. The cyanides, which he says are quickly formed when hot carbide is exposed to nitrogen, are readily decomposed by superheated steam to form ammonia. He therefore recommends maintenance of low temperature in the generator, letting the carbide fall into a large volume of cold water which will leave the aluminum nitride and the cyanides undecomposed, and by which the small quantity of ammonia liberated may be absorbed.

For the purification of acetylene many suggestions have been made and several processes proposed. Oderheimer uses something like the Laming mixture of sawdust and iron compounds which seems to reduce the tendency of the gas to give smoky flames but it does not remove the phosphorus compounds. Lunge and Cedercreutz easily remove the hydrogen phosphide by passing the gas over wet calcium chloride and afterwards through lime to hold back the chlorine. Frank finds that the phosphorus and sulphur compounds may be reduced to a minimum by washing with acid metallic salt solutions and Pictet uses, in succession, the following liquids: (1) a very concentrated solution of calcium chloride, (2) solution of lead compounds, and (3) sulphuric acid. All the solutions are cooled to —16° C. at which temperature he finds the impurities are absorbed while the acetylene is not.

It is held that the thoroughly purified acetylene will form combinations with neither copper nor other metals, and is even less poisonous than ordinary illuminating gas ; but in presence of air or moisture combinations with metals are likely to be formed, and these substances should therefore be carefully excluded.

Both Pintsch Co. and Pictet have specially studied the sensitiveness of the gas when compressed to heat and shock. The Pintsch Co. filled a vessel whose joints were soft soldered, the pressure within being six atmospheres. When heated to 200° the solder melted and the gas issuing from the opened joint burned quietly ; but another vessel with hard soldered joints, likewise filled with pressure of six atmospheres, laid upon a burning wood-pile, ultimately exploded with the greatest violence. Pictet cools the gas to —20° C. as it comes from the gasometer, separates the moisture, forces it at eight atmospheres through a cooling system, bringing it to —80°, at which temperature and pressure it becomes liquid. It is stated that the containing bombs which, by the way, were fitted with brass cocks, were pierced with rifle bullets, struck with mallets, and hurled against rocks without causing explosion.

But the Pintsch Company recommends, as a further measure of safety, that for use in railway lighting the gas be mixed with oil-gas in the proportion of thirty per cent. of the former to seventy per cent. of the latter. Claude and Hess find that while acetone will dissolve at 15° C. about twenty-five times its volume of acetylene. if the pressure be increased to twelve atmospheres it will hold 300 times its volume. That is to say one liter of acetone is capable of holding 300 liters of acetylene or the quantity ordinarily liberated from one kilogram of carbide. The acetylene thus held will be given off with release of pressure until solubility at atmospheric pressure is reached. The mixture is said to be practically non-explosive, and therefore much safer than liquefied acetylene, but it is suggested that before use it be washed to remove the accompanying acetone.

Concerning the relative efficiency of acetylene as a practical illuminating agent much has been said. Hubou finds that ordinary burners of different lighting powers consume of acetylene per candle-power hour:

	Acetylene consumed. Liters.
Burners of 1 to 2 c.p.	8
" " 2 to 5 "	7.5
" " 5 to 10 "	7.0
" " over 10 "	5.6

Pictet offers a table of comparison of cost of the various sources of light used in Paris based upon prices of illuminating material as follows: Calcium carbide, 0.4 franc per kilogram; acetylene, 1.5 francs per cubic meter; petroleum, 0.97 franc per kilogram; illuminating gas, 0.3 franc per cubic meter; incandescent electric light, 1.0 franc per kilowatt hour.

The ratios of cost of these different materials as used to acetylene are respectively as follows: Normal lamp, 4.4 : 1.2; petroleum round-wick lamp, 7.7 : 3.6; Argand gas burner, 3.8 : 1.2; Paris burners, 6 : 6 to 9 : 11.2; Wenham lamp, 5.1 : 5.5; Welsbach light, 2.6 : 3.4 and 3.6 : 5.6; incandescent electric, 3 : 1.2.

Wedding's table of comparisons illustrate these same relations as they appear in Germany and will be of interest:

	Candle-power.	Heat per candle-power. Cal.	Cost per hour.
Illuminating gas-slit burner	30	66.5	6.4
" round burner	20	50.	3.2
" regenerative burner	111	18.4	6.5
" incandescent burner	50	10.	1.6
Spirit incandescent lamp	30	10.6	2.0
Kerosene	30	32.0	2.2
Kerosene incandescent lamp	40	13.75	1.0
Acetylene	60	8.9	5.4
Electric light incandescent	16	2.59	2.9
" " arc light	600	0.37	15.5

These figures are less favorable to acetylene than those of Pictet.

Ten French factories are making calcium carbide for the production of acetylene gas and four are being built. France next year will produce three thousand tons of the carbide, worth $75 a ton, exclusive of the cost of packing. Two villages in France are lighted wholly by acetylene gas. Each house in these villages has its own gas plant, just as bicyclists in this country make their own gas from the carbide. The lighting power of acetylene is fifteen times that of coal gas. For the same amount of light it costs 50 per cent. less than coal-gas.[1]

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[1] This paragraph is quoted from a despatch to one of the current daily journals. M.

Krämer discussing the production of benzene as a by-product of the coking industry says that the yield of 4500 to 5000 tons in a single year caused the price to fall to twenty-five marks per 100 kilograms, the quantity being three times as much as is obtained in Germany from gas-tar. To utilize the excess he recommends its admixture with alcohol, adding ten per cent. (10 : 1) for use in incandescent lamps. Frank states that the Charlottenberg Gasanstalt found that when added to illuminating gas of thirteen to fourteen candle-power, four grams sufficed to increase the lighting capacity, one candle-power. Schimming and Jaeger, found that mixed water-gas and coal-gas required seven to eight grams benzene for one candle-power increase. Krämer however showed that water-gas free from methane will not hold benzene effectively.

The discovery of Nernst that when calcium and magnesium oxides are heated they become tolerably good conductors of electricity and that when further heated by the transmission of a current they become highly incandescent is most interesting. Even at the highest white heat they are not softened or materially changed. If the carbon filament be covered with a layer of magnesium oxide and enclosed in a vacuum globe the oxide becomes heated and finally incandescent. Such a rod gives with a current of 0.25 ampère and 108 volts a light of twenty-eight Hefner candle-power or one candle-power per watt while the ordinary incandescent lamp consumes three to four watts per candle-power. The initial heating of the magnesium oxide presents difficulties, and the life of the filament is questioned.

Auer von Welsbach utilizes in his incandescent light the hitherto unknown property of osmium *in vacuo* and in a reducing gas mixture to resist liquefaction or volatilization even at the volatilization points of iridium or platinum. Since the light emission of a glowing body grows much more rapidly than its absolute temperature it is held that good light effects should be obtained by the use of osmium filaments instead of carbon filaments in the incandescent lamps. The same observer finds that platinum wire will not melt even at the most intense white heat if covered with only so much as one-tenth millimeter of thorium oxide. It would therefore appear that even more easily melting bodies than osmium may be used for the preparation of filaments to stand particularly high temperatures.

Altogether the status of the illumination problem has materially changed within the year, and decided progress may be expected in the very near future.

In the production and recovery of the nitrogen compounds, some progress has been made. It is reported that in England the production of ammonia as sulphate in 1897, from different sources respectively was as follows :

	Long tons.
From gas works	132,724
" iron "	17,729
" shale "	37,153
" coke "	10,624

It is also reported that in Europe the production in 1898 will exceed 375,000 tons of sulphate against the production of 330,000 tons in 1897. Of this, Germany and Austria produced 100,000 tons; 46,000 tons from Eschweiler and the Saar, 40,000 tons from upper and lower Silesia and Austria, and 14,000 tons from gas works.

These must remain for some time the principal sources of the ammonia compounds, yet we must expect that the utilization of other waste products may contribute at least a small share. Thus, Pieper and Fellner propose to collect the gases issuing from the dry distillation of nitrogenous organic matters as well as those from nitrogenous coke. One-third of the nitrogen passes off, they say, with the hydrocarbon gases, and the remainder is removed by superheated steam in an apparatus specially designed for the purpose.

In the fixation of atmospheric nitrogen, attention has already been called to the results of Lord Rayleigh which showed that if the nitrous compounds generated in the atmosphere be promptly removed from the sphere of action of the spark by means of an alkaline solution the yield becomes attractive. During the past year Berthelot has continued his researches in this direction. His investigations into the fixation of nitrogen by carbon compounds and particularly the carbohydrates under the influence of electrical tension such as prevails in the Siemens tubes are well known, and are of the highest interest. He has now extended them to the study of the alcohols, ethers, phenols, and similar compounds and finds that under the influence of the electric spark in an atmosphere of nitrogen containing vapors of the substances named, nitrogen is fixed and hydrogen liberated; in other words true substitution is effected, the quantity of nitrogen fixed varying with the different compounds. The action is here doubtless similar to that occurring in the Otto apparatus already mentioned and illustrates further the influence of the electrical tension upon the intensity of chemical action, adding thus to the future applications of the current.

In the production of the cyanides from atmospheric nitrogen, but little by way of suggestion or improvement has been offered. Blackmore proposes to produce cyanides, ferrocyanides, and thiocyanates by fusing together a mixture consisting of metallic sulphides and carbides, and passing nitrogen gas through the mixture. He recommends an alkaline sulphide and iron carbide for the purpose. Petschow melts alkali in a crucible and introduces nitrogen mixed with hydrocarbon gases, such as acetylene, or with carbon dust, to the melt through an opening in the cover. He avoids excess of carbon, but does not limit the quantity of nitrogen or ammonia used. Excess of the latter is to be collected in acid, and the cyanide recovered by well-known methods. Colné, of Pittsburg, proposed a method for production of cyanide and ammonia in the following steps carried on in a closed alkali furnace: (1) burning of air and gas, (2) dissociation of liquid hydrocarbon, (3) dissociation of alkali and formation of cyanide. In connection with this, decomposition of the cyanide with superheated steam for producing ammonia. Caro passes free nitrogen over barium or calcium carbide alone, or over these substances mixed with alkali and carbon, the whole heated in a clay retort or tube to a dark red heat. Rossel and Franck heat the carbides of aluminum, magnesium, zinc, or iron in presence of nitrogen to form the corresponding nitrides.

Conroy, Hurter, and Brock convert the thiocyanate into cyanide by heating together in an autoclave under pressure, calcium thiocyanate and ferrous chloride, but preferably the thiocyanate and reduced iron in excess, with the following reaction:

$$Fe(CNS)_2 + 2Fe = Fe(CN)_2 + 2FeS.$$

The residuum is treated with soda-lye and leached to obtain sodium ferrocyanide; or the mass is treated with weak hydrochloric acid, the hydrogen sulphide collected, the ferrous cyanide washed and treated with alkali. If the ferrous chloride is used in the first process the residue from the soda leach is treated with hydrochloric acid, and the resulting ferrous chloride used as indicated.

The United Alkali Company have utilized the reaction of nitric acid with the thiocyanates for the production of pure cyanide. The solution of 20 to 30 per cent. thiocyanate is mixed with an excess of nitric acid and forced in fine spray into a closed vessel containing hot water and fitted with a stirring gear. Air must be vigorously excluded from the apparatus, the thiocyanate is broken up, sulphuric acid is formed, cyanogen gas is liberated and the latter after being washed to free from nitrous fumes is absorbed in an alkaline solution or cold water.

Nithack, of Nordhausen, undertakes the production of nitrogen compounds by the electrolysis of water charged with air, making use of an observation of Davy to the effect that under such conditions ammonia will be formed at the cathode and nitric acid at the anode. He therefore electrolyzes water charged under pressure with air and claims to so obtain ultimately a strong solution of ammonia salt.

What seems to be an improvement in the manufacture of oxalic acid has been patented in the United States and England. Woody matter is dried and heated, *in vacuo*, to 70° C. to remove air. Hot alkali liquor is then run in upon it, the vacuum maintained, and temperature raised to 180° C. The progress of the operation is controlled by testing a sample from time to time. When the digestion is complete oxidizing substances such as hydrogen dioxide, sodium dioxide, air, or ozonized air, are introduced while the vacuum is maintained. The resulting product is treated according to the usual process of oxalic manufacture. The industrial value of the process remains to be determined.

The growing prejudice of the French medical fraternity in favor of higher value of white wines for human consumption has stimulated their production and to the extent of removing the color of wine from red grapes. To this end Martinaud extracts the juice thoroughly, aerates it until it is completely decolorized, filters it to remove the precipitated coloring-matter, and ferments the resulting liquid. The special advantage of the white wine thus made is not stated.

Buchner, of Tübingen, has made the interesting discovery that the process of alcoholic fermentation is not purely physiological and part of the vital function of the yeast plant, but is due to the influence of an enzyme produced within and secreted by the living cell. He mixed beer yeast with fine sand, ground the mass till the whole was well reduced, subjected it to pressure of 500 atmospheres, and so obtained 450 grams of juice, which was yellowish, transparent, almost clear—but sometimes somewhat opalescent—having pleasant odor and containing carbon dioxide and not a little coagulable albumen. Among other enzymes there were present invertin and maltose and glycogen hydrolyzing ferments besides oxybases. When sugar is added to the juice fermentation is set up much more quickly than with fresh yeast and the liberated gas is pure carbon dioxide. Its action upon sugar is lost in two or three days, but in presence of sugar it continues five or six days. It may be dried without losing its power. Yeasts differ considerably as regards the juices they yield and the juices of some cells have no fermenting power.

More interesting and valuable to the industry is the discovery of Dr. Calmette of Lille, France, of a micro-organism which has the power of converting starch directly into alcohol without the previous intervention of malt or other hydrolyzing agent. He practically applied his discovery in a distillery where 250 kilograms of grain gave 10,000 liter per cent. of alcohol (100 liters of absolute alcohol). If this operation and result can be duplicated it will eliminate from the distillery the use of malt and greatly diminish the cost of production of alcohol. The yield of alcohol reported is attractive being about as high as is ordinarily obtained in the distilleries of either this country or Germany and the new ferment will doubtless receive serious attention from those directly interested in the development of the spirit industry.

The promise of the production of spirit from moss, peat, waste woody matter, etc., has not been fulfilled, and the results of Stenberg, of von Felitzen and Tollens, and of Simonsen give but little encouragement to the industry. Tollens, ascribes the unexpectedly low yields of alcohol obtained in each case to the presence of pentoses in the crude materials, which, although converted by the acid treatment, yield products incapable of alcoholic fermentation. Thus Tollens in his study of peats made determinations of the total reducing substances and of the pentoses and found that the difference between the results corresponded closely with the fermentable carbohydrates as indicated by the alcohol obtained. And Tollens' results correspond closely with those obtained by Maercker.

The process of Fritsche for producing alcohol from ethylsulphuric acid obtained from washing the ethylene from coke-oven gases has not further developed notwithstanding the possible low cost of the product and this has been ascribed to the limited supply of the raw material. It is estimated that the total theoretical production from this source could not exceed 5,000,000 gallons of absolute alcohol; but it has been suggested that a further source of ethylene would be possible in the reaction between calcium carbide in an acid solution containing zinc or some other metal, whereby it is expected that the nascent hydrogen and nascent acetylene might combine with formation of the compound sought. The resulting ethylene was to be treated after the method of Fritsche for production of alcohol. The cost of operation of this process would doubtless preclude its use even with very low cost of calcium carbide and therefore of acetylene. It is impossible to say however what the future may have in store for us in this particular, for with cheap acetylene on one hand, with cheap hydrogen from the electrolytic processes of Latchinoff, Garuti, or of Schuchert & Co., together with electrical apparatus of Otto for intensifying chemical activity, cheap and abundant ethylene may still be possible. The suggestion will doubtless be attractive to those most closely interested.

In every direction industrial progress is suggestive, and we may expect advancement in all directions with increasing intensity. Commercial artificial indigo, commercial artificial silk, commercial mercerized cotton in its various forms, the new colors and medicinal substances from the carbon compounds, new concentrated nutritive substances, synthetic albumen, the various toxines and extracts of animal matters of therapeutic value, all claim a large share of attention; and so do hundreds of other substances and processes in which the principles of chemistry find application to human needs but they must, for such discussion as this, be left to other hands and for other occasions in the hope that neither may be wanting to fill the gaps necessarily left by the present effort.

WM. MCMURTRIE.