TECHNOLOGICAL CHEMISTRY.

ITS DEVELOPMENT DURING THE LAST FORTY YEARS.

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THE representatives of chemistry, general and physical, inorganic and organic, have striven in noble emulation to surpass each other in the number and importance of their discoveries. From the laboratories great and small, official and private, the results of research have flowed like the rivulets which, irrigating the well-watered fields, come together in brooks, then in streams and in rivers, bringing fertility to the habitations of men in the valleys. An abundant harvest has been raised on these watered plains, a harvest which has been enthusiastically consumed by the people.

The harvest, the reward of scientific research, the abundant fruit of the patient work of the mind, consists of the applications which contribute to the well-being of the people. This is why technical chemistry is the worthy companion of abstract research in our science. It should prosper when research is flourishing, and the additions to chemical technique, during the last forty years, are a striking proof of the correctness of this assertion.

About the time when the German Chemical Society was founded a period of far-reaching transformation began in industrial chemistry. The industry of mineral acids and alkalis, based on the Leblanc process—the only one which could boast at that time of the title “great chemical industry”—still adhered to its stereotyped operations and to the dependency of its series of steps, one upon the other, but the young Titan which was destined to struggle with and cause its complete rehabilitation—the Solvay process for the production of soda by means of ammonia—had come into existence and was already developing. About 1870 this process appeared to have reached a productive stage, and it was recognized that the possibility of obtaining soda independently of the Leblanc process would break up the whole continuity of this great chemical industry. It was still protected, however, by the close dependence on it of the production of hydrochloric acid and from this the making of chlorine by the sulphate process, and by the advantages offered by the soluble product of its raw soda in the preparation of caustic soda. In truth, these two circumstances prolonged the life of the Leblanc process for several decades and are responsible for the fact that even yet it has not entirely disappeared.

Toward 1860, almost simultaneously with the development of a commercial process for the production of soda by ammonia, came the inauguration of the potash industry at Stassfurt, which was founded on the fortunate discovery of the deposits of salts there, under the fertile influence of Liebig's wonderful researches.

To the preparation of potassium chloride from carnallite and sylvinites soon were added the preparation of bromine, of potassium nitrate by the use of sodium nitrate, and the manufacture of potash by the Leblanc process, without any danger here of a concurrent process with ammonia. Finally, a successful process was developed for the utilization of part at least of the magnesium compounds which were present in the salt deposits, although the successful extraction of all the magnesium chloride made in the potassium industry is to-day still in the category of unsolved problems.

The year 1870 saw the rejuvenation of the century-old industry of oil of vitriol, the fuming sulphuric acid, whose small content of sulphuric anhydride no longer sufficed for modern needs.

In place of the product obtained by distilling vitriolic schists came synthetic sulphuric anhydride, prepared by the catalytic combination of sulphurous anhydride and oxygen, and the pyrosulphuric acids. The new process of manufacture was to influence and transform the whole sulphuric acid industry to a great extent. It was possible to apply it with advantage more than a quarter of a century later, when the modern process appeared.

The last two decades of the nineteenth century were characterized by the development and application with exceptional rapidity of electro-technics. In the field of chemistry, this new phase of industry voiced itself in the development of electrolytic methods of operation. In the field of electro-metallurgical processes, the most important of which are the preparation of aluminium and the electrolytic refining of copper, which are closely followed by the manufacture of calcium carbide and carborundum, the question of the electrolytic decomposition of alkaline chlorides has

been a most warmly discussed problem. The difficult problem of preparing membranes which are more sensitive, and at the same time more resistant, was solved almost simultaneously by three processes, that of Griesheim, that of Castner-Keller, and that of Ausig, which are close rivals in their effectiveness and boldness of invention. With these a new era has begun in the production of caustic alkalis, and also in the chlorine industry. The old process for the production of chlorine has disappeared along with the ingenious methods of Weldon and Deacon. Chlorine, once so costly, is produced in such abundance as to provoke a feverish search for new applications for it. By the side of and often in the place of the venerable chloride of lime we find to-day liquefied molecular chlorine put up in transportable form in steel bottles.

Finally, the production of alkali metals on a large scale should be counted as one of the most important results of modern electro-chemical technology. The same reaction in a form suitable to technical methods which once in Davy's hands led to the discovery of these metals—the electrolysis of alkaline hydrates—has shown itself to be the best and least costly method of manufacture for these strongly reactive bodies, one of which especially, sodium, has rapidly become of extensive application in a technical way. By its aid in particular, it has been possible to produce potassium cyanide free from cyanates, which has contributed to the success of the cyanide process for refractory gold ores.

Such a metamorphosis of inorganic chemical technology as has been briefly described would not have been conceivable if greater and greater quantities with their continually decreasing prices had not found a continually increasing market. The same fact along with the natural increase of needs generally has produced in the case of organic chemistry an even more striking and remarkable transformation and development than in inorganic technical processes.

We all know in a general way that the old industries of brewing, distilling, sugar making, and starch making, of the production of fatty bodies and of foods, all of which are connected with agricultural work, have flourished remarkably in the last forty years and have become of very great importance. They owe their most important progress to the aid of modern biological research. But besides these, other industries operating on organic substances have sprung up and prospered, which were formerly entirely unknown.

A lively interest attaches to the chemical application of wood which has not only allowed a particularly profitable use of our forests, which is coming more and more into evidence, but has also led to a simple separation, almost analytical in its nature and carried out on a large scale, of the components of lignine, one of which, however, the incrusting medium, remains to this day a chemical enigma.

The extraction of an almost pure cellulose from wood has placed the paper industry on a new footing and has obviated the necessity of our limiting the production of printed matter for want of paper. It has led to the discovery of a number of other useful applications of cellulose, of which I will mention only the preparation by various methods of new artificial textile fibers analogous to silk.

Wood can be worked chemically, however, in another way than by the separation of its content of cellulose. I refer to the process of dry distillation. The very primitive preparation of carbon and wood tar of the old days has developed during the last forty years into a very highly perfected art of wood distillation, which has obtained most important commercial results with decomposition products formerly entirely neglected—methyl alcohol, acetone, and acetic acid. The attempts, first without result, but later crowned with success, to free the ligneous acetic acid from the empyreumatic bodies obtained with it have resulted in the fact that the greater parts of our demands for acetic acid are now supplied by the distillation of wood. This industry received a still further impetus in 1890 by the introduction of a process for the preparation from methyl alcohol of formaldehyde, the production of which has enormously extended since the extraordinary variety of uses to which this new product can be put has been recognized.

Another remarkable method for the treatment of wood, fusing it with alkali for the production of oxalic acid, has not developed, but rather has diminished in importance during the forty years under consideration. It has been replaced by the synthetic method of pre-

paring this acid, as well as of formic acid, by means of carbon monoxide contained in generator gases. Formic acid can be prepared so advantageously in this way that it is competing with acetic acid in many of its applications.

The commercial utilization of hydrocarbons of the methane series is brought out in two industries—the distillation of lignites and the refining of petroleum. Both of these industries have shown an extraordinary increase in their extent and have displayed numerous marked improvements in their production. Among the latter the desulphurization of fetid petroleum of the Ohio type by distillation over copper oxide should be considered a technical achievement of high rank.

The development of coal distillation and the treatment of tar affords a particularly important and interesting example of progress. When this society was founded only one form of distillation of coal was recognized—its application to the manufacture of illuminating gas, which dates from the end of the eighteenth century. This distillation was carried on at a low temperature and furnished the entire amount of tar produced, the tar which is so important in the recently developed color industry. In 1880 the output of tar began to be less abundant, a fact caused not only by the constant increase in its use in the production of tar dyes, but also to a great extent by the far-reaching transformation of the gas industry, which on account of extended and ingeniously interpreted experiments had been developed into an entirely new process, characterized by the employment of high temperatures of distillation. The momentary embarrassment which fell on the dye industry led to the creation, far-reaching in its consequences, of a new industry—distillation for coke, which saves from destruction the riches contained in the by-products of coke manufacture and which frees for a long time the dye industry from any lack of raw materials.

Among the products derived from coal tar may be mentioned anthracene, carbazol, the xylenes and the cresols, coumarone and pyridine, substances whose systematic manufacture is only forty years old and which have found a steady commercial application. Of many of the other of the tar derivatives, some have been only recently discovered, while others have been rendered more available than heretofore.

It is to the improvement in its methods of operation, especially in the apparatus, that the industry of tar distillation owes the thoroughness with which its products may be separated from such a complex mixture as goes to make up tar. Column stills, filter presses, and processes such as vacuum distillation are the means which have enabled the modern tar industry to attain its present position.

The most striking example of an industry working hand in hand with scientific research, profitably applying all its results and influencing them in its turn, is afforded by the manufacture of coal-tar colors. It is almost impossible to touch in these few words on the most important stages of the triumphal progress of this industry.

We may say that the foundation of the German Chemical Society was coincident with the date when the newly founded color industry was emancipated from empirical methods and turned toward scientific synthesis. The first great success obtained through this agency was the creation of the alizarin industry, whose later development has surpassed all expectations. The recognition of the close connection between constitution and properties of coloring matters found its practical application in the introduction of azo dyes, which not only brought into the industry an extraordinary variety of colors, but accustomed the dye chemist to develop almost quantitative methods of work. In the group of phthaleins were found not only some of the most striking coloring materials, but also some of the most permanent, thus refuting the theory, not proved, but then current, that artificial colors were ephemeral in the same proportion that they were brilliant. Equally permanent dyes were found among the eurhodines, safranines, oxazines, indulines, and thionines, the study of which is so intimately bound up in that of nitrogen chains and the joining of nuclei. The discovery by a mere chance of a fast alizarin blue, so important from a technical point of view, likewise carried in its wake great consequences for scientific chemistry, for the investigation of the composition of this dye led to a synthesis, capable of general application, of the derivatives of quinoline. In a like manner the explanation of the constitution of rosaniline was very productive in allowing the synthesis of numerous

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new compounds, among which are found some of the most beautiful and valuable dyeing materials.

The appearance of substantive azo colors, and finally of those known as "sulphonated dyes," has not occasioned the opening of any new avenues of scientific investigation. These two accomplishments, however, are of the greatest importance in that they have provided new methods for dyeing and printing and have completely revolutionized these two ancient industries.

Lastly, we may mention the new class of indanthrene colors in which are united clear tints with an hitherto unknown resistance to all destructive influences.

It is the synthesis of indigo, however, that we must hail as the most brilliant of all conquests in the field of coloring materials. We can still recall the day when the great event in chemical history was made public and when every hand was extended in congratulation for this masterpiece of scientific research. The struggle for a solution of this great problem cost twenty years of assiduous labor, but, once solved, how well the new product of synthetic indigo has stood the test beside the natural product backed by several thousand years' use.

There is no hope that this industrial triumph in the coloring field will ever be surpassed. It is none the less certain, however, that this industry has not yet attained the limit of its development. Our reviews in the future will still record many achievements bearing witness to the uninterrupted development of this interesting and manifold branch of technology.

We may consider the manufacture of synthetic medical preparations as an offshoot of the color industry which sprang up in the period we are considering and which has already earned a position of its own. What brilliant results have been accomplished in this field, also. What a beautiful gradation of development from complex insufficiency to simple perfection can be witnessed in comparing kairine and thalline on one side and antipyrine, phenacetine, and aspirine on the other. What a progress in the regulation of physiological functions is evidenced in chloral hydrate and veronal. What pains has not synthetic chemistry soothed by its

activity in this field, what ills has not it assuaged.

The industry of artificial medicines is only one of a vast circle of varied activities which we are in the habit of grouping together under the collective term of preparation industries. To properly appreciate this industry with all its ramifications is impossible. Nevertheless I cannot help mentioning the appreciable growth of a branch of this industry which is almost as old as this society. This is the manufacture of chemical products and preparations for photography, whose expansion has been closely connected with the development of scientific photochemistry and with the introduction and popularization of dry photographic plates with their proper processes of development.

No less interesting are the chemical and technical aspects of the perfumes newly created and developed during the last forty years. This field, which is completely developed along its principal lines at the present day, was still unexplored at the time when the German Chemical Society was founded. Its expansion is reflected more completely in the pages of our transactions than anywhere else. Step by step nature has been imitated in its creations, and in this field perhaps more than anywhere else the synthetic chemist has taken paths which follow those of nature.

Among the synthetic industries we should count the technology of explosives, although here it is a matter less of constructing molecules than of storing up energy in a form easily liberated. In this industry great progress has been recorded, almost all of which depends on the utilization of the facts expressed by the law of Sprengel, expounded about forty years ago, and on the employment more and more of safe explosives which can be detonated only by an initial ignition, in place of bodies themselves explosive. The possession of such explosives and the application to the phenomena of explosion of modern methods of observation have alone made possible the new orientation in ballistics, which is well known to all of us.

If we consider all this technological progress that I have mentioned and much more which I must refrain from describing, we must agree that as far as appli-

cations are considered our science has reached a high state of development. But just as scientific research, in spite of the abundance of results, still presses forward, so will technology not stand still, but will continue to attack more and more difficult problems.

When this society was founded there was already, it is true, a very well-developed series of chemical industries, but their activities were limited almost entirely to the extraction, purification, and transformation of natural products. An industry operating synthetically on a large scale is a development solely of the last forty years. To-day we are striving for even more lofty ends. We have dared to lay a hardy hand even on the great processes of nature in seeking to influence them according to our needs. It is this that we behold in the great factories where many are striving to utilize the nitrogen of the air. Many methods have been proposed to attain this end; the combustion of nitrogen to its oxides and the transformation of it into cyanogen or ammoniacal compounds have been used.

All these methods are practicable and will all probably be productive of results. Which of these results will be the most important it is for the future to decide. In all of them, however, is this characteristic feature—they do not rob Nature of its amassed treasures, nor do they wish to imitate her creations; they aim merely to assist her in one of her greatest processes, the circulation of nitrogen. If we succeed in influencing this phenomenon, we will also in a measure control that other which is so intimately bound up with our fortune or misfortune, the course of life. We will force the earth to greater fertility, to an increasing habitability.

In such a task Nature herself should be our ally. The savage force of the water which falls from above carries out the chemical work which we call upon it to perform, and a day is beginning to dawn when it will be not only a pretty metaphor, but one of peculiar force and meaning, to speak of the fertile influence of the brooks which ripple down from the mountains into the valleys where stand the habitations of men.

LIQUID AIR AND OXYGEN. SOME NEW USES.

SOME interesting industrial applications of liquid air and of oxygen made from liquid air were noticed in a recent paper read by Mr. George Claude before the Society of Civil Engineers of France.

Commercial plants for the production of liquid air by the Claude process or by the Linde process exist in various European countries (there is also quite a large one in this country using the Linde process, in Buffalo, N. Y.) Their chief product is compressed oxygen, and the principal applications of the oxygen are autogenous welding with the oxy-acetylene flame, cutting of metals with the oxy-oxy-acetylene flame, and the manufacture of artificial precious stones.

But the price of oxygen thus produced is still comparatively high, as Mr. Claude points out, on account of the large expense for compressing and bottling the oxygen gas in cylinders and the shipping expenses. The cost of the oxygen gas would be greatly reduced if it were required in large quantities on the spot. An essential item in the cost is represented by the pressure to which the air under treatment must be compressed. This pressure is given by Claude as 18 atmospheres for apparatus producing 100 cubic meters (3,530 cubic feet) of oxygen per hour, and is estimated as 10 atmospheres for 1,000 cubic meters (35,300 cubic feet).

At present 1 cubic meter (35.3 cubic feet) of oxygen is obtained per horse-power-hour in apparatus producing 50 cubic meters (1,765 cubic feet) per hour. The figure of 1.25 cubic meters (44 cubic feet) of oxygen per horse-power-hour is guaranteed by the Société de l'Air Liquide for apparatus producing 200 cubic meters (7,060 cubic feet) per hour; and the figure of 1.75 cubic meters (62 cubic feet) of oxygen per horse-power-hour represents the hopes of the manufacturers for apparatus producing 1,000 cubic meters (35,300 cubic feet) per hour.

A plant for the yearly production of 50,000,000 cubic meters (1,765,700,000 cubic feet) of pure oxygen requires not more than 20 meters by 30 meters (65 feet by 98 feet) floor space and 15 attendants.

For a plant to be erected with apparatus producing 200 cubic meters (7,060 cubic feet) of oxygen per hour, Mr. Claude's company has guaranteed that the cost of producing 1 cubic meter (35.3 cubic feet) of oxygen, including amortization, will be slightly more than 0.6 cent; that is, figured on the basis of the cost of 0.4 cent per horse-power-hour (an exceedingly low price which is thought to be justified because blast-furnace gases are used in driving the gas engines for power production at that place).

A very important and interesting experiment on a large scale is soon to be made by a Belgian iron and steel plant, the Société d'Ougrée Marihay, with respect to the enrichment of the air with oxygen for the blast in one of their blast furnaces and converters.

At the conclusion of his lecture Mr. Claude showed a number of experiments, like the liquefaction of oxygen in contact with liquid nitrogen; the condensation of atmospheric air on the outside of an iron bottle containing liquid nitrogen; further, the fact that coke maintained at the temperature of liquid air absorbs gases with such energy that it is possible to realize rapidly a vacuum of less than one-tenthousandth of a millimeter. Mr. Claude also subjected a current of illuminating gas fed to a burner to the action of liquid air; the result was a modification of the flame which assumed the characteristic appearance of the hydrogen flame. This experiment indicates the possibility of a cheap process for making hydrogen by partial liquefaction of water gas. Other experiments illustrated the ease of recovery of volatile substances in chemical industries by refrigeration, such as ether and alcohol in the manufacture of artificial silk, and the facility of extracting neon and helium from the atmosphere.

In this connection it is interesting to report a lecture delivered November 18th, 1909, before the Polytechnic Association of Berlin, by Dr. H. Erdmann on the technical application of liquid oxygen. (Chemiker Zeitung.)

Dr. Erdmann first discussed briefly the chemical properties of the liquid gas and also described a modified arrangement for investigation of its purity by means of the aerometer. It is possible to utilize liquid oxygen at the same time for three purposes, namely, to utilize its cooling effect, the pressure, and its chemical energy.

The consumption of liquid oxygen is much greater than is generally supposed, although we have no accurate statistics regarding it. Three methods of manufacture are in use. By the Brin method, barium oxide (BaO) is heated in a current of atmospheric air to form barium peroxide (BaO₂). The air current is then stopped, and the barium peroxide reheated in a partial vacuum, whereby oxygen is given off. By the second, the electrolytic method, the gas is obtained from water, but this is economical only when there is use at the same time for the hydrogen generated simultaneously with the oxygen in equivalent proportion. Electrolytic cells for this purpose have been devised by Schuckert, Garuti, Schmidt, and others. The third

method, based on the fractional distillation of liquid air, is now very largely employed in Europe. For operation on a large scale the cascade principle, which was first used by Pictet in 1877, is used to advantage. The lecturer mentioned briefly the processes of Cailletet, Kamerlingh-Onnes, Claude, Hildebrand, and Linde.

Altogether there is annually produced in Germany 8,000 cubic meters (282,500 cubic feet) of oxygen (meaning evidently oxygen gas at atmospheric pressure) by the Brin method, 342,000 cubic meters (12,070,000 cubic feet) by the electrolytic method, and 2,200,000 cubic meters (77,700,000 cubic feet) by the fractional distillation of liquid air. The average cost for one kilogramme of fluid oxygen amounts to about 10 pfennigs.

The oldest use found for oxygen is in explosives, oxygen cartridges not being dangerous. In recent years oxygen has found use in the production of light. In this connection was mentioned the Nürnberg light, which it has been found consumes very little illuminating gas and produces less heat than the ordinary gas lamp. It is also more hygienic since the oxygen is supplied to the flame and is not, therefore, taken from the air, thus contaminating the latter. In metallurgy oxygen finds many uses; for instance, in the oxy-hydrogen and oxy-acetylene flame for autogenous welding and cutting of metals. Oxygen is also used in the production of fused quartz (silica) vessels. Oxygen used in medicine must have the highest purity; this accounts for the higher price. According to Michaelis, oxygen, which is 96 to 97 per cent pure, costs 6 marks (\$1.43) per cubic meter, while 99 per cent oxygen costs 10 marks (\$2.38).—Metallurgical and Chemical Engineering.

The Baku papers state that the exploitation of the well water—i. e., the water that accompanies the naphtha in the bore holes, which consists of a concentrated salt brine—is about to be commenced. It contains iodine and bromine, both of which can be extracted and the remaining liquor evaporated for salt. Attention is also called to the water in the Grosny wells, particularly in the Daghestan district, where, during the boring, highly concentrated brine was found—with the naphtha—rich in iodine. The idea of treating these waters is not of course new. Mr. K. I. Liseko long ago called attention to the rich content of salt and iodine they held, and which were run into the sea from the Baku wells. But for want of means they had to be let go on.