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THE COMMERCIAL MANUFACTURE OF OXYGEN.

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Oxygen is a colourless gas, having neither taste nor smell, and is the most widely distributed and important element in nature.

In the year 1774 oxygen was discovered by Priestly, and also about a year later by a Swedish chemist named Schule.

The modern science of chemistry may be said to date from the discovery of oxygen, and on account of its practical value in chemical industries, much time and money has been spent in endeavours to discover some method by which it could be produced commercially in a pure state, and at a reasonable price, and it is only in recent years that this has been achieved, and oxygen put on the market at a price undreamt of a few years ago.

There were a great many methods of producing oxygen, and between the years 1850 and 1890 about sixty patents were taken out in Great Britain alone for the production of oxygen, but the majority of these processes never passed beyond the laboratory stage, and could scarcely be considered as commercial methods.

CHLORATE OF POTASH METHOD.

One method of producing oxygen, which has been known for more than a hundred years, and which has been used for producing oxygen in small quantities, was the **chlorate of potash method**, which was as follows:—

Oxygen was evolved during the decomposition by heat of potassium chlorate, but the temperature required was so high as to melt the salt, and cause ebullition, and as this reaction, when once started, was uncertain, and

danger of explosion due to the violent ebullition was always present, it was only in cases where the purest oxygen was required that it was prepared from the salt alone.

In ordinary practice, one-eighth to one-fourth of its weight of manganese dioxide was mixed with the potassium chlorate, and the mixture placed in a pear-shaped retort, which was very slowly raised to a dull red heat, the effect of the manganese being that the oxygen was given off at a lower and safer temperature than when the potassium chlorate was used alone.

The gas made in this manner was not so pure as that evolved from the salts direct, and contained more or less traces of chlorine.

This method was very expensive, and there was always an element of danger present in its manufacture. This process is now very rarely used, and will probably be only of historic interest in a short time.

Brin Process.—Another method of producing oxygen, which more than held its own against all other methods, was that known as the **Brin** or **Barium Oxide Process**. This process was patented in 1885 by two French brothers named Brin, and depended on the fact that when barium oxide ($Ba. O$) is heated in air it combines with oxygen, forming barium dioxide $Ba. O_2$, and when this latter is heated more strongly, or under diminished pressure, it gives up oxygen, again becoming $Ba. O$.

Barium oxide is a mineral substance closely resembling lime in its properties, and is found in lead districts. Oxygen was produced commercially by the barium process in 1886 in London, and the plant consisted of the following units:—

A furnace, with a series of retorts, called the producer.

A series of purifiers.

An air pump.

An automatic gear, consisting of a series of three-way cocks, valves and other appliances, so arranged that at any required period they were automatically reversed by an action controlled by the air pump.

Air from which the carbon dioxide had been removed was pumped under a pressure of about 10lbs. per square inch through retorts containing barium oxide, heated to a temperature of 1350 degrees Fah. When the issuing gas was no longer approximately pure nitrogen, the air current was stopped, and the residual nitrogen in the retorts was pumped out until the pressure had fallen to about 2lbs. per square inch.

The barium di-oxide then gave off much of its oxygen, which was collected in the gas holder. In large plants two complete units were employed, so that a continuous flow of oxygen passed into the gas holder.

The renewal of material was a small item in the cost of production, and it was the only process successfully applied for the production of oxygen for commercial purposes. Fig. 1 shows a view of a barium plant. The barium process has been superseded by the electrolytic and liquid air processes.

The Electrolytic Process.—This process has been employed on the Continent for some time, and as electric power is now very cheap, and many improvements have been made in the electrolytic apparatus itself, the production of oxygen and hydrogen from water is now thoroughly established on a commercial basis.

There are a good many different makes of electrolytic plant, but in all apparatus for the electrolysis of water two essential conditions must be observed, viz., reduction to a minimum of the electrical power required, and perfect separation of the two gases.

Water, as an electrolyte, is a poor conductor, and caustic soda or caustic potash is generally added to improve its conductivity and facilitate decomposition. Oxygen produced in a good electrolyser has a purity of from 95 to 97 per cent., and the hydrogen a purity of from 97 to 99 per cent. The impurities are, of course, hydrogen and oxygen, and these residuals are largely eliminated by passing the gas through tubes containing heated palladium pumice in the form of an electric furnace, before finally passing the gases into the retrospective gas holders.

An electrolytic plant for a large output of oxygen per 24 hours requires very much more motive power than a liquid air plant of the same capacity, so that, unless a good market can be obtained for the hydrogen without heavy cost incurred in its distribution, a liquid air plant is by far the most economical proposition.

Where oxygen is the gas required, there is no doubt that the liquid air plant is the cheapest and most economical, and if I might venture to say so, the most interesting, as we enter the region of low temperatures, the fancy fringes of refrigeration, where such substances as alcohol, mercury, etc., which were once considered refractory to freezing, lose all right to this reputation, as they become hard as stone before the temperature of liquid air is reached. Mercury freezes at 40 degrees C.

Further, by submitting liquid air to fractional distillation, Professor Ramsay and his collaborators found **neon** and **helium**, and also isolated **krypton** and **xenon**, the latter two being inert gases absolutely unique on account of their enormous atomic weights, 80 and 160 respectively. Of these rarer gases, helium is the most refractory to liquefaction, boiling at 269 degrees C., and it is only recently that Professor Kamerlingh Omnes has succeeded in liquifying it.

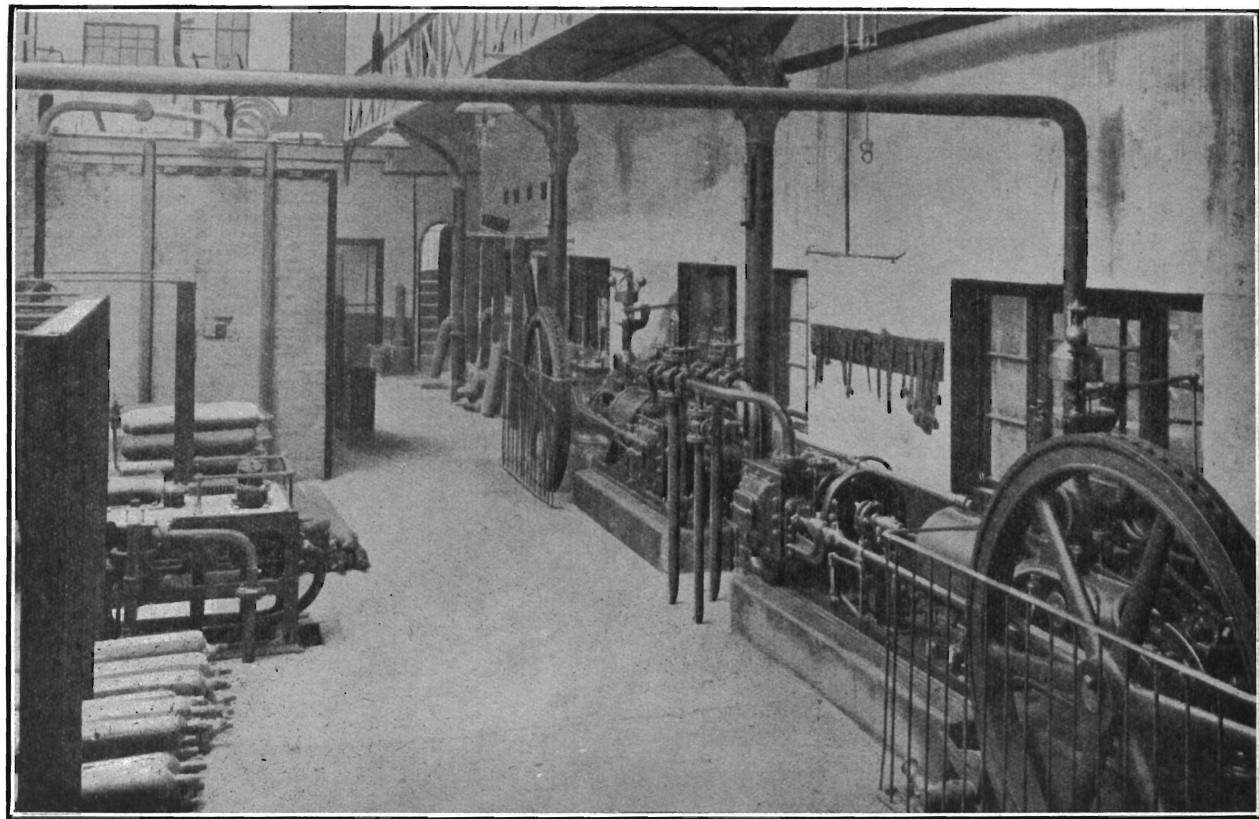


Fig. 1

I fear, however, that I am drifting from my subject this evening, and will, therefore, try and describe to you briefly the method of producing oxygen by what is known as the "Liquid Air Process."

Liquid Air Process.—The first adaptation for the manufacture of oxygen by the liquefaction of air occurred in 1895, but it was not until 1902 that the manufacture of oxygen on any commercial scale was attempted.

This process, however, was only able to extract two-thirds of the oxygen contained in the atmosphere, but the French scientist, Claude, by a refinement of this process, made it possible to extract nearly all the oxygen from the atmosphere without any increase of work, and Claude was the first to utilise part of the energy contained in the compressed air by expanding it in a cylinder to perform external work, thus creating a greater degree of cooling than can be obtained with simple internal expansion.

It is worthy of mention that an Englishman, Dr. Hampson, took out a patent in 1895.

Hampson's apparatus is without doubt the simplest of all liquid air appliances. It consists of a two-stage air compressor, designed to bring the air to a pressure of from 150 to 200 atmospheres; the compressed air, freed of its moisture and carbonic acid by means of potash, passes through an expansion valve, after having traversed a copper tube of very fine bore and great length, bent into a spiral.

The apparatus depends on a means by which a moderate amount of refrigeration, produced by the expansion of a gas, may be accumulated and intensified till it reaches the point at which the gas becomes liquid under atmospheric pressure.

The cold developed by expansion in the first expanded gas is thus communicated to the on-coming compressed gas, which consequently expands from, and, therefore, to a lower temperature, than the preceding portion. It communicates in the same way its own intensified cold to the succeeding portion of compressed gas, which in its turn is made colder, both before and after expansion, than any which has gone before.

This intensification of cooling goes on until the expansion temperature is far lower than it was at starting, and the effect is so powerful that even the small amount of cooling, due to the free expansion of gas through a throttle valve, may be made to liquify air without using other refrigerants.

Hampson's apparatus, when the compressor is working at from 150 to 200 atmospheres pressure, begins to liquify air in from 6 to 10 minutes after its admission, and makes about $1\frac{1}{2}$ litres of liquid air per hour. No ice, salt, carbonic acid, or other refrigerant is required, and it produces a perfectly clear liquid, which requires no filtering.

I believe that one of Hampson's liquifiers was supplied some time ago by my firm to the Sydney University.

Until a few years ago there was no great demand for oxygen in large quantities in Australia, but with the advent of oxy-acetylene welding and cutting, and the application of oxygen to many metallurgical operations, a demand arose for large quantities of pure oxygen at a reasonable price, which would permit of its application profitably to these processes.

Most of the oxygen used up to this time had been imported, and consequently the price was high. To overcome this difficulty, an oxygen factory, equipped with the most modern and up-to-date liquid air plant,

supplied by the British Oxygen Co., Ltd., of London, the pioneers of the compressed gas trade, was erected at Alexandria, New South Wales, by the Commonwealth Oxygen Co., Ltd., under the writer's supervision, and oxygen placed on the market here at a price which made its use a paying proposition to those employing it.

This plant is driven by a Diesel engine, and consists of the following units:—

A four-stage belt-driven air compressor.

A lime purifier for removing the carbonic acid from the air.

High pressure driers, where any moisture in the air after compression is absorbed.

A forecooler, where the compressed air is cooled considerably before entering the separator.

The separator, where the air is liquified and the oxygen separated from the nitrogen.

There is also a CO_2 refrigerating machine, which cools part of the forecooler, and a gas-holder, into which the oxygen is discharged prior to being compressed into cylinders by the oxygen compressors.

There is also a complete water circulating system, consisting of belt-driven pumps, some of which draw the cooling water from the tank of a spray cooler outside the main building, and after circulating it round the various machines, pumps it through the spray nozzles of the cooler, so that the water is used over and over again, and only the slight waste from evaporation has to be made up.

It may interest you if I describe each individual unit of the plant more fully, so that what takes place at the different stages in the process may be easily followed.

The Diesel Engine.—This engine is one of the well-known two-cylinder, four-cycle engines, made by Messrs. Mirrlees, Bickerton & Day, Ltd., of Stockport, running at 250 revolutions per minute, and developing about 100 B.H.P. at this speed. The fuel used is crude oil, and the main storage tank for the fuel oil is underground, in a building some 30 feet from the main machinery building, and the fuel is forced by compressed air from one of the starting receivers of the engine into an overhead settling tank inside the main building, and the amount of oil in this overhead tank is shown by a pointer on an indicator board placed near the engine.

The oil then flows by gravity from this settling tank to a small tank near the engine, where it is finally filtered before being drawn in by the fuel pumps.

The fuel oil is strained three times from being emptied into the large storage tank until it reaches the engine, and any water in the oil is abstracted in the overhead settling tank.

The Lime Purifier.—The air is drawn through this by the suction of the air compressor, and the purifier consists of a cast iron tank, about eleven feet square, in which there are several layers of slaked lime, each layer of lime resting on wooden grids. A canvas blanket is placed on the top layer of lime, and so fixed in position that no lime can be drawn through by the compressor.

The lid of the purifier is made of sheet iron, and its sides rest in a water-sealed lip on the cast iron sides of the tank, so that no air, except what has been drawn through the lime, can reach the compressor.

The air enters at the bottom of the tank, and passes up through the lime, the outlet being on the top side of the canvas blanket.

The carbonic acid is removed from the air in passing through the purifier.

The Air Compressor.—This is a two-crank belt-driven tandem four-stage air compressor, running at 180 revolutions per minute, and capable of compressing the air to a final pressure of over 2,000lbs. per square inch.

The first and second stages are on one side, and the third and fourth stages on the other side, the pulleys, fast and loose, being placed between the cranks.

The air after each compression is cooled to normal temperature by being passed through pipes or coils round which water is circulating. The pistons are lubricated by oil forced in by special ratchet feed lubricators. This is a special oil, with a high flash point, and the internal lubrication is a point which requires most careful attention.

All valves, suction and discharge, require to be kept in perfect order, as any serious letting back of pressure is liable to cause trouble.

Each stage is fitted with safety valves, and pressure gauges record the pressures in the various cylinders, so that a sudden increase of pressure in any stage is provided for, and the fourth stage, or high pressure gauge, is connected to an electric alarm bell, which can be made to ring at any desired pressure, and thus warn the attendant of any sudden increase of the final pressure.

After leaving the air compressor, the air, now at a pressure of 2000lbs. per square inch, is passed through a number of cylindrical shaped vessels, containing a special calcium chloride, which absorbs any moisture in it. These driers, as they are called, are blown periodically to remove the moisture collected in them.

The air now passes into the forecooler, which is a cylindrical-shaped vessel, containing internal coils, and it is here that advantage is first taken of the cooling effect of two gases at different temperatures, flowing in different directions, as the incoming air pipe is surrounded in the top portion of the forecooler by a pipe, through which nitrogen is passing to the atmosphere, and in the lower portion by a pipe containing carbon di-oxide, which is the expansion coil of a CO_2 refrigerating machine, the air leaving at the bottom of the forecooler where the expansion pipe from the CO_2 machine enters. The CO_2 machine is driven by belt from a pulley on an extension of the engine shaft.

In the forecooler the air is not only cooled well below the freezing point of water, but any traces of moisture remaining in the air are frozen, and thus dry air enters the separator, where any traces of moisture would cause choking in the coils of the counter current inter-changers.

The separator is that part of the plant where the liquefaction of the air and the separation of the oxygen and nitrogen takes place.

The separator can best be described, I think, by means of a diagram, and Fig. 2 is a sectional elevation of a separator.

The thick black line represents the outer wooden casing, inside of which is the rectifying column A. The base is also constructed of wood, and of hexagonal shape, and contains the distilling or vapourising chamber B. All clearance spaces are packed with insulating material, so as to prevent external heat from penetrating.

The separators at Alexandria Works are packed with a form of asbestos wool, which has also the advantage of being fireproof. C is the counter current inter-changer, which consists of a large copper spiral pipe,

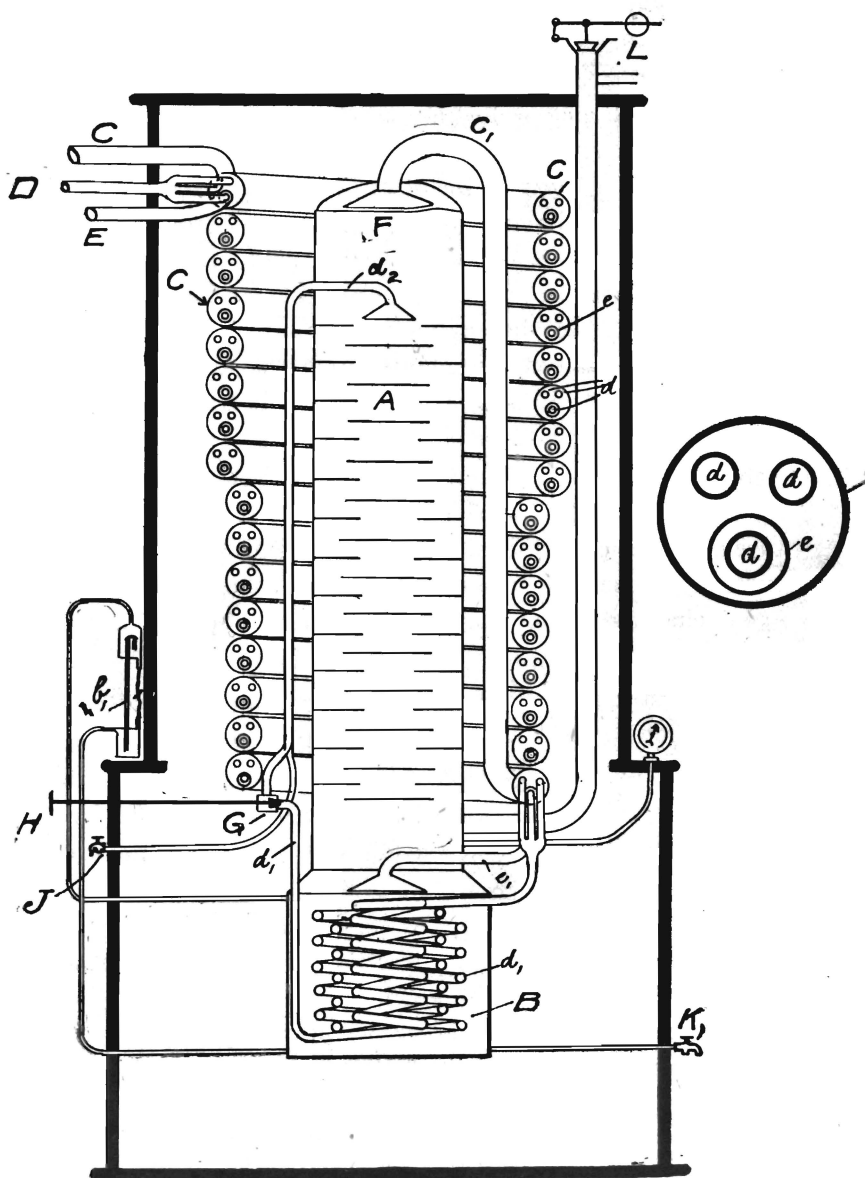


Fig. 2.

and containing three small copper pipes d , one of which is enclosed in a larger pipe, e , as indicated in the larger diagram. C , is an extension of the main spiral pipe to the top of the rectifying column A, with a funnel, or bell mouth, F, projecting within A. e , is an open bell mouthed extension of the pipe C at the top of the vapourising chamber B.

The pipe coiled in the vapourising chamber is connected at one end with the small pipes d , inside the counter current interchanger. The other end of this pipe is connected to the valve G, to the expansion side of which another pipe, d_2 , is connected, which pipe enters the rectifying column near the top, and is fitted with a rose end, as shown.

The working of the apparatus really consists of two operations:—

(1) The cooling down and production of the liquid, and

(2) The separation of the oxygen from the liquid.

The cooled air at high pressure coming from the fore-cooler enters the pipe D, into the three small pipes d of the counter current interchanger, passes down these pipes, through the pipe coil d in the vapouriser, to the expansion valve G, which is regulated by a handle H, and the air expands from the high pressure to a low pressure (3 or 4 lbs. per square inch), and passes out through this low pressure through the rose d_2 into the top of the rectifying column, from which it can escape only by the outlets c , and e , into the counter current interchanger, in a reverse direction of flow to the incoming high pressure air, leaving it through the pipes C and E.

It is at this valve G that the Thomson-Joule effect, which is that applied in Hampson's patent, takes place, and regenerative cooling occurs in the counter current

interchanger, where the incoming compressed air parts with some of its heat to the outgoing air, which has become colder by the temperature drop on expanding.

This cooling effect goes on cumulatively until a temperature is reached at which the expanded air begins to liquify, and the liquified air collects round the coils in the vapouriser B. The amount of liquid in B is recorded in a glass tube *b*, enclosed in a pressure equalising circuit, as indicated.

When the whole apparatus has been cooled down nearly to the temperature of liquid air, the liquid accumulates rapidly in B, and the pressure of the incoming air reduced by further opening the valve G. Until this stage is reached, any separation of the oxygen and nitrogen which has taken place is due solely to fractional evaporation.

As the liquid accumulates in B the compressed air inside the coil transmits some of its latent heat to the liquid, which is thereby evaporated, while the compressed air is itself liquified in proportion to the amount of heat thus extracted, the vapours thus produced flowing upwards, through the rectifying column, in which the liquid is flowing downwards. The temperature gradient necessary for efficient rectification rapidly becomes established in the column, and the second stage is reached in which the apparatus produces oxygen.

The temperature gradient depends on the different boiling points of nitrogen and oxygen. Nitrogen boils at 77.5 degrees absolute, and oxygen at 91.5 degrees absolute.

The liquid air discharged into the top of the column is at a temperature of about 81 degrees absolute, and the nitrogen, being more volatile than the oxygen, at once begins to boil off, and thus the maximum cold is automatically created at the top of the column.

For the same reason, the nitrogen contained in the original liquid air in B is liberated by latent heat from the compressed air, so that the temperature of the liquid in B becomes higher as the oxygen portion increases, and thus the highest temperature is also automatically established at the bottom of the column.

When all the nitrogen has been expelled from B, the liquid air passing down over baffle plates in A meets the rising vapours of oxygen, and an exchange of material takes place. At each stage some of the rising oxygen is condensed, and some of the nitrogen in the down-coming liquid is evaporated, while the liquid gradually rises in temperature, until by the time it has reached the vapouriser it is practically pure oxygen.

The gas which passes off through the funnel F is nearly all nitrogen, at a temperature of about 14 degrees lower than that of the oxygen at the bottom of the column. The oxygen which rises in the column A to effect the material change with the nitrogen of the down-coming liquid air, is carried back to B with most of the oxygen contained in the original liquid.

The excess of oxygen continually gathering at the bottom of the apparatus is drawn off as a gas through the pipe *e*, into the pipe *e* of the counter current interchanger, so that the gases drawn from both the top and the bottom of the apparatus are made to abstract heat from the incoming compressed air.

The pressure at which the gases escape from the apparatus is 4 to 5 lbs. per square inch, the nitrogen being utilised to cool the incoming compressed air in the top portion of the forecooler.

There is a relief valve, L, on the expansion side, and J and K are test cocks for liquid air and liquid oxygen.