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PROBLEM OF LIQUID AIR.[1]

by P. Kapitsa, member of the Academy of Sciences of the U.S.S.R.

(Translated from Planovoe Khozaystvo, 1939, no. 2, p. 73-80)

Before describing the liquid-air plant which we have developed at the Institute for Physical Problems, I wish first to discuss the reasons for this work and the theoretical considerations which served as a basis for its development.

Air was first liquefied long ago - in 1877 - by Cailletet and Pictet. At first, however, liquid air had no practical importance. The development of this was hindered by the extreme complexity of the apparatus devised by Pictet (although even from the modern point of view, the cycles used by him allow air to be liquefied efficiently)

Only in 1895, when Linde and Hampson practically simultaneously developed a simpler apparatus for obtaining liquid air, did it begin to penetrate into laboratory practice. Even though the Linde apparatus, based on the Joule-Thomson effect, is of low efficiency, it was nevertheless widely used owing to its simplicity. There was a time when almost every large laboratory had it. In some places it has been preserved and works even to this day.

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Investigation of the properties of liquid air led to one remarkable discovery, made almost simultaneously by Linde and Bali in 1899. It was shown that nitrogen boils at a temperature 12.8 deg. cent. lower than oxygen. Consequently, when liquid air evaporates, more nitrogen evaporates from the very start and the remainder becomes enriched in oxygen. Linde saw that this could be used as a means for obtaining pure oxygen by multiple distillation (as is done, for example, in the petroleum industry and in other fields where it is necessary to fractionate two liquids having different boiling points) And so, at the beginning of the last century [sic.], Linde began to construct a series of plants with the practical aim of obtaining liquid and gaseous oxygen.

As soon as cheap oxygen was achieved, a demand for it arose, chiefly in autogenous work. With the increase in autogenous work, the demand for oxygen kept increasing and therefore more and more powerful plants were built for obtaining gaseous and liquid oxygen.

With oxygen available in large quantities, industry started to apply it to different uses and whole large fields have now been developed which use oxygen, and there is a whole series of important fields whose development depends on the procurement of cheaper oxygen. Industrial demand for oxygen is easily explained by the fact that it is needed in the combustion process, which is the basic and the most important field of national economy. In addition to oxygen, which is directly necessary for burning combustibles, four times as much inert nitrogen is present during combustion in air, not only unfavorably lowering the combustion temperature but also causing loss of heat (the nitrogen carries it away when leaving the furnace). Calculations show that in a number of cases even partial enrichment of air with oxygen can considerably increase the intensity and economy of technical heating processes. From this arises the modern demand for oxygen and oxygen-enriched air for metallurgy, power economy, gasification of coal and oil, - a demand amounting to tens of thousands of cubic meters per hour. No less a demand also exists for nitrogen free from oxygen, a basic product in the nitrogen-compound chemical industry, called upon to satisfy the urgent needs of agriculture in the form of nitrogenous fertilizers.

Finally, with the development of the processes for decomposing air, other, very small, fractions of rare gases included in the air began to be removed. Among these, krypton and xenon should be especially noted, they being the best fillers for incandescent electric lamps. The efficiency of the lamps after being filled with krypton and xenon increases 20-30 per cent. and the cost of obtaining these gases is more than covered by savings in electric energy.

Such a great industrial demand for the gases in the atmosphere presents science with the problem of more economic production of these gases, both from the viewpoint of reducing the cost of apparatus (capital investment) and from the point of view of efficiency (energy losses).

Thus, in order to obtain oxygen and nitrogen from the air, these gases have to be separated. With the help of thermodynamics we can calculate the theoretical minimum work needed for this separation. Simple calculation shows that this is the work needed for the isothermic compression of each of these components from their partial pressure to the normal. It can be shown that a minimum of 0.068 kWh. would have to be expended to separate the oxygen from one cubic meter of air.

This minimum however, refers to the expenditure for obtaining oxygen from the air. Might it not be possible to obtain oxygen from some other source with a lower expenditure? This question must be answered in the negative. Atmospheric oxygen is in a free state, while in other forms it is in a compound state.

Therefore, extraction of oxygen from the air is theoretically most economical.

But concerning the production of oxygen from the air, it is necessary to state that fractionation at low temperatures is the only practical method at present. This fractionation can be carried out reversely. Therefore, if in practice this fractionation involves large losses of energy, it is not because the principles of the method are themselves at fault but because of the imperfection of the apparatus. It is possible to develop theoretical cycles in which the fractionation of oxygen and nitrogen will be completely reversible, i.e. the whole process will proceed with minimum energy losses.

In actual practice in the better mass-production plants abroad, 0.5 kWh. are expended to produce one cubic meter of oxygen, i.e. 8 to 9 times the theoretical minimum. (No such large plants exist in this country as yet, and so we can not use our own data but have to depend on references in the literature) Thus the coefficient of useful work of these plants is 0.14.

In starting my work, I asked the question: why do all these cycles have such a low efficiency? What is the matter here? What steps in the fractionation process unprofitably use up such an enormous amount of energy?

Fractionation of oxygen and nitrogen is performed at very low temperatures, at -194 deg.cent. At this temperature, which differs very sharply from room temperature, it is difficult to avoid heat losses. And it was shown that just to cover these losses in existing cold plants 0.2 to 0.3 kWh. are required, i.e. 3 to 4 times as much as for the separation itself.

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After this was established, we found what we had to combat this first. This shows that the apparatus which replenishes the lost cold is extremely inefficient and the chief attention must be devoted to making the frigorific machines more efficient.

The following question then arose: why is it then that modern frigorific machines are so inefficient, what are the reasons for the losses in the refrigerating processes? Obviously this question is important to the problem of obtaining cheap liquid air, because the chief amount of cold is used in its production.

This is how we approached the problem of obtaining cheap liquid air. Before describing how this problem was solved, we pause for a general description of modern liquid air plants.

To obtain air in a liquid state, it must be cooled to -194 deg.cent. Compressed air in the refrigerating machines is made to do external work through expansion: this work is absorbed. It has been proved that the cooling of the air is equivalent to the work produced by it.

The construction of an efficient machine which would work at low temperatures proved to be extremely difficult. This problem was attacked for many years. The best solution was found by Heylandt. His machine is quite similar to a steam engine, but compressed air is introduced in place of steam: it performs work (pushes the piston) and cools. It does not expand to normal pressure in these machines, however, but only to 8 to 10 atmospheres and does not cool to the temperature of liquid air, but only to -150 deg. In order to cool the air 44 deg. more to the temperature at which it becomes liquid, it becomes necessary to take advantage not of mechanical work but of the internal work of the gas, which is done in the

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following way. Air, compressed at 200 atm., is cooled to -150 deg. by means of the Heylandt expansion machine and then it is allowed to expand to normal pressure. Upon expanding, it cools further to such an extent that part of it goes over into the liquid phase.

The chief source of loss under present conditions is the poor efficiency of the expansion engine. The reason for this low efficiency is the technical difficulty of building these engines. The difficulty consist in the inability to provide low-temperature liquid lubricants for a piston moving tightly, with low friction, in a cylinder. Heylandt avoids this difficulty thus: the cylinder and piston are at room temperature and the air, cooled during its stay in the cylinder, does not have time to lose the cold by contact with the walls. This can be done without large losses only when the volumetric heat capacity of the gas in the cylinder of the pressure reducer is large. In the Heylandt pressure reducer, therefore, in order that these losses may not become excessively large, the expansion is from 200 to 8-10 atmospheres and the available work of expansion from this pressure to the normal is lost. Consequently, the corresponding cold is lost, the most valuable part since it is produced at the lowest temperatures.

Thus all these processes can not be performed at low pressures. Therefore, to make up the losses of cold and to maintain a sufficient amount of fractionable liquid, an additional aggregate of high pressure is put into air-separation plants, and in practice, owing to the difficulties of working with high pressures, in spite of the fact that a smaller part (up to $\frac{1}{10}$) of the whole mass of air passes through the aggregate of high pressure, more is often produced than by the aggregate of low pressure. This is explained by the use of high-pressure piston compressors, which are exceedingly cumbersome.

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Is it not possible to do without these high pressures? Is it not possible to find an air-liquefaction process with a coefficient of useful work great enough to cover cheaply the losses during cooling and to use only low pressures?

First of all it is necessary to answer the question, under what conditions is such a process in general possible. It is obvious that if we want to work at pressures of, say, 5-6 atmospheres, we have to achieve -196 deg.cent. in one cycle, i.e. we have to obtain all the cold by adiabatic expansion, since the internal cooling effect can only be utilized in a gas which is highly compressed. The only machine in which it is theoretically possible to obtain such a low temperature is the turbine.

The turbine also has other advantages. It requires no lubrication: the bearings on which the rotor turns may be carried outside by means of a long and thin shaft and kept at room temperature while the turbine is turning in the cold air. This idea is not new in itself - it was first suggested in 1898 by Rayleigh. Forty years have passed, however, and turbines have not yet been used to any great extent for obtaining cold. Linde in Germany and Claude in France attempted to use them; turbo pressure reducers were also proposed in this country. But the coefficient of useful work of all the types experimented with proved to be very low (0.6) Such a low efficiency at low pressures can not be counted upon to produce sufficient cold for cheap liquefaction of air.

The following question was proposed: why do turbines have such a low coefficient of useful work? Does this follow inevitably from the fact that they work at low temperatures, or is it simply due to faulty design, the result of an incorrect conception of the machine? Up to now this question was not brought up; the most prevalent type of impulse turbine was used for obtaining the cold. An impulse turbine is nothing more than a nozzle from which gas escapes, and a series of blades upon which this gas impinges. The kinetic energy of the impinging gas is thus transformed into rotary energy.

We approached the investigation of the possibility of obtaining the best coefficient of useful work from a turbine from a purely theoretical point of view, not entering at first into the details of design. We strove to make clear - the losses in any turbine are the functions of what? Is it the function of the velocity of motion of the gases, the revolving speed of the blades, and so on and so forth?

It appeared that the losses in a turbine decrease with a decrease in the kinetic viscosity of the gas working it. Kinetic viscosity equals ordinary viscosity divided by the density of the medium. And since air at low temperatures is very dense while at the same time its viscosity is not very different from that at the ordinary state, therefore the kinetic viscosity of air at low temperatures is very small, for example 20 times less than that of steam. This circumstance was apparently not ordinarily taken into consideration.

Since all turbine calculations were made for working with steam, certain losses which depend on the density of the gas were disregarded. But, as our theoretical investigations showed, precisely these losses will be particularly great in frigorific turbines. Among these, the chief is the loss caused by the irregular movement of the gas under the action of centrifugal forces.

With this clarified, our problem was to utilize to advantage, as in hydraulic turbines, these centrifugal forces, which cause trouble and greatly lower the efficiency.

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Thus we came to the conclusion that gas at low temperature should be treated not like steam but rather like water, and to construct a turbo pressure reducer modeled, not according to a steam turbine, but rather according to a hydraulic one. In this connection, however, we must not lose sight of the fact that a gas nevertheless remains a gas, with a whole series of properties characteristic of a compressible medium. Our problem, therefore, was to construct a turbine in which the energy was to come from two sources: the impulse action of the stream of gas and the utilization of the centrifugal force. This would result, in spite of the remaining losses, in a doubling of the power. These theoretical concepts had to be tested in practice. Therefore a turbine was constructed at our Institute which combines the principles of an impulse and of a hydraulic turbine.

This turbine was very small. Its rotor weighs approximately 250 gr., but passes about 600 cu.m. 21,100 c.ft of air per hour. These small dimensions of the turbine are explained precisely by the fact that air at low temperatures has a great density. On the other hand, the compressor supplying air to this turbine weighs 3.5 tons. This gives an idea of the relative dimensions of the revolving mechanisms, turbines and piston compressors. While the lower pressures can be produced by turbo compressors of considerably smaller dimensions, greater pressures up to 200 atm. have to be produced by piston compressors - their construction in frigorific plants involved great expense.

Our experimental turbine did not work immediately. As is always the case in experimental work, difficulties arose from unexpected sources. The first serious difficulty was the inability to obtain steady movement of the turbine. And this is very important, because with a high number of revolutions the speed of individual parts of the rotor attains 200 m. per sec.,
656 ft/sec.

which is not far from the velocity of small shot fired from a gun; meanwhile, the space between the rotor and the casing must be made very small (0.15 mm.) in order to avoid losses. With such a small play and such high speeds, every vibration of the turbine was very dangerous.

In solving the problems of steadiness of revolving turbines, we came across a series of phenomena whose explanation gave not only the possibility of making our turbine run absolutely steadily, but may possibly also have an effect on making even larger steam turbines run more steadily and lead to the decrease of various allowances and tolerances and in this way also contribute to increasing their efficiency.

Tests of the turbine constructed at the Institute showed that our theoretical reasoning was entirely justified. Its coefficient of useful work was above 80 per cent. in spite of its small dimensions (It should be noted that the coefficient of useful work in large turbines is always greater than in small ones, because in them the ratio of the surface area to the volume is less and therefore there is less loss, since the amount of gas worked is proportioned to the volume and the loss — to the surface area through which heat transfer occurs)

We use the turbine to obtain liquid air. The plant where it works operates as follows: air passes through a dust filter into the compressor where it is compressed 6 to 7 atm. The compressed air passes through a water tube cooler and degreaser and enters the valve chamber of the regenerators. Past the valve arrangement, the stream of compressed air enters the regenerator, consisting of a tube filled with a large amount of metallic strip, called the packing, and from there passes into the

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turbine where it expands and cools. It then returns through another regenerator, to the packing of which it gives up its cold. The direction of the air is changed every half minute by a reversing valve. Outside air enters the regenerator through which the cold stream has just passed and the air enters the turbine already pre-cooled. As a result of subsequent repetition of this process, the air leaving the turbine cools to a temperature low enough to liquefy the compressed air entering the condenser. The liquid air in the condenser goes to a collector, from which it can be drawn off. The vaporized gas joins the general stream coming from the turbine before the condenser, so that its cold is used for liquefaction further on.

One of the advantages of using air at low pressures is the following: in addition to safety, greater reliability and the possibility of using turbo-compressors for compression, preliminary removal of carbon dioxide and moisture from the air is unnecessary; it is known that when using regenerators, which can be used only at low pressures, we need not worry too much about this. The admixtures of carbon dioxide and water are precipitated in the regenerator with the entering stream of air, but are again blown out by the outgoing stream. This simplifies and lightens the plant considerably.

As a result of all these advantages, we not only obtain a more economical liquid air plant, but also a much cheaper one than the ordinary type, since it weighs 8 to 9 times less.

Such an experimental plant has been in use for 9 months in our laboratory and continuously supplies the Institute with liquid air.

Our plant begins to liquefy air within 18 to 20 minutes after starting from rest, while the process of liquefaction in the usual plants starts only after some hours.

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Thus there is every reason to believe that one of the problems of obtaining cheap cold, an important step in the manufacture of gaseous oxygen. by using this turbine, will be considerably advanced.

The next problem of the Institute is to apply these methods to obtaining gaseous oxygen. It should also be noted that in the given case the attainment of cold at low pressures will apparently also make it possible to simplify and make more efficient those cycles which are used for fractionation.

From the editor: The new method of making liquid air by using a special turbine, described above in the article by academician P.L.Kapitsa, deserves close attention from planning and economic organizations. Liquid air is used principally to obtain oxygen and nitrogen. Also the separation from air of such rare gases as krypton and xenon is of great importance to national economy.

The problem of manufacturing cheap gaseous oxygen is one of the important means of technical progress for many branches of socialistic industry. The use of oxygen as powerful means of intensifying chemical processes is constantly increasing. The effectiveness of using oxygen is indicated in the metallurgical industry (blast-furnace process, open hearth furnaces, converters) the result being a speeding up of the metallurgical process, a decrease in fuel and an increase in the production of aggregates. In the chemical industry the use of oxygen in a number of industries (sulfuric acid, soda and others) greatly increases the productivity of the factories. The use of oxygen in industry allows simplification of the technological process and intensification of production. It is unnecessary to speak of the importance of oxygen to autogenous welding and cutting, which have been widely developed in the Soviet Union.

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Special mention is made of the importance of oxygen to the gas industry in the USSR, and particularly to the young industry, unique in the world, of underground gasification of coal. Insofar as the active rôle in the process of underground gasification of coal is played by oxygen, just so much will the increase of its quantity hasten the process, sharply increase the production capacity of underground gasification stations, and increase the heating possibilities of the gas. In addition to the fact that oxygen is the most important factor among the conditions for underground gasification of coals for intensification and rationalisation in the production of high-caloried industrial gas, its importance is also conditioned by the fact that the use of oxygen allows most easily the overcoming of difficulties arising from the exploitation of coal in exceedingly wet locations. In the surface gasification of coal and particularly in the gasification of local low-caloried types of fuel, the use of air-oxygen blowing also causes very important increases in the production of gas and a sharp improvement in its quality.

The solution of the problem of obtaining liquid air also represents an important advance in the production of gaseous oxygen.

The scientific-technical solution of new methods of producing liquid air and its subsequent step - the production of gaseous oxygen on the basis of considerable cheapening of the corresponding processes upon their instillation in industrial practice, will undoubtedly find use in many branches of socialistic economy.

Foot-note.

1. Stenographic abridgement of a paper presented at the meeting of the presidium of the Academy of Sciences of the USSR on Dec.25, 1938.

Illustration.

Plant for producing liquid air.

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