

# LIQUID AIR AND THE LIQUEFACTION OF GASES

## A PRACTICAL WORK GIVING

The entire history of the liquefaction of gases from the earliest times of achievement to the present day—the biography of the great investigators—the manipulation of liquid air and liquefied gases—experiments with the same—the modern uses of liquefaction processes and of their products—the utilization of the nitrogen and oxygen of the air, the rare gases, helium, argon and neon, and their utilization, and the latest developments in this field of industrial science, are also treated.

BY

T. O'CONNOR SLOANE, Ph.D.

Author of "Arithmetic of Electricity," "Electricity Simplified," Etc.

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## CHAPTER X.

## SIGMUND VON WROBLEWSKI AND KARL OLSZEWSKI.

Wroblewski's life—Banishment from his native country—Early scientific work—His association with Olszewski—Study of Cailletet's methods—Their apparatus—Defective position of the hydrogen thermometer—Liquefactions of oxygen, carbon monoxide and nitrogen—Ethylene data—Solidification of carbon bisulphide and alcohol—Determination of the critical pressure and temperature of oxygen—Liquefaction of hydrogen—Use of a thermoelectric thermometer—Electric resistance of metals at low temperatures—Two liquids from air—Olszewski's individual work—Apparatus for producing liquid oxygen in quantity—Comparison of platinum resistance and of hydrogen thermometers—Determination of hydrogen constants.

As a serious investigator in the realm of the liquefaction of gases, no one can be cited who surpassed the Polish scientist Sigmund von Wroblewski (pronounced Vroblevski). He was born in Grodno, Poland, in 1845. Grodno is a province which went to Russia in the partition of Poland and figures in the final partition of 1815 as part of Russia. The kingdom of Poland, as arranged by the Congress of Vienna at the same time, remained as a separate kingdom and intact, although its monarch was the Czar of Russia. Then there was a long series of political disturbances and bloodshed, culminating in the disturbances of 1861-64, and Russia succeeded by

the most arbitrary enactments and severe measures in suppressing the insurrections and in assimilating the so-called kingdom of Poland.

Wroblewski took part in the uprising as a Polish patriot, and was sent to Siberia in 1863, where he spent four years. His friends had influence, and managed to obtain his release from exile, to the extent of being allowed to live in an obscure Russian town. Eventually he was released from surveillance and went to Germany, visiting Heidelberg and Bonn, meeting Kirchoff and Clausius. He had a cosmical theory which was not received by either the physicists of Heidelberg or of Bonn with any encouragement. At the University of Berlin he consulted Prof. Helmholtz, who started him to work on physical investigation touching his new theory, and he completed two years of work under the many-sided and brilliant German. He published papers bearing on gases which received the honor of attracting the attention of Clerk Maxwell. His principal work on high pressure and low temperature applied to gases dates from his knowledge of the work of Cailletet on the same subject. He spent some time at the École Normale, in Paris, and saw and studied Cailletet's work. He had as associate Karl Olszewski (pronounced Olshevski), in the writing of the initial of whose Christian name a certain amount of confusion obtains, as it is sometimes written K, for Karl, and sometimes C, for Charles. The association between the two in their early work of 1833, and thereabout, is very intimate. In *Wiedemann's Annalen*, 1883, is published an article which gives the full account of their first important work

in the liquefaction of gases. The authorship is given a dual form. The title reads in translation, "On the liquefaction of oxygen, nitrogen, and carbon monoxide, by Sigmund v. Wroblewski and Karl Olszewski." The article, it is impossible to believe, was written by anyone but Wroblewski, but when in its course anything is to be attributed to a single investigator, the expression "*einer von uns*" ("one of us") is always used.

Wroblewski died in 1888. As early as 1884 he predicted that liquid air would be the refrigerant of the future. His emotions, had he lived to see what has been done in the liquefaction of air, can only be imagined. The principal reason for his belief in the capabilities of liquid air was that it did not have to be prepared like carbon dioxide, sulphur dioxide, ethyl chloride, or ethylene, that the atmosphere gave an inexhaustible supply of matter adapted for the function of refrigeration and for use in a cooling cycle.

Wroblewski, in the early days of the liquefaction of gases, in 1885, pointed out the method of the future. In the light of what has been since then accomplished, a translation of his remarks from the *Wiener Sitzungsberichte* reads almost like a prophecy:

"The essential step forward which should be made with regard to the extension of the method is to change it so that we may be prepared to pour oxygen as we pour ethylene to-day. It is my conviction that the thing will only be successfully carried out when we return to Pictet's method, and by cycles of various liquefied gases make a cascade of

temperatures whose last step will produce the stream of liquefied oxygen."

It is precisely by carrying out such a line of work that Dewar won fame for himself and the Royal Institution.

The carefully prepared article in *Wiedemann's Annalen* is an example in its way of how a scientific paper should be written. There is in its aspect and tenor such sincerity and so careful an avoidance of anything like self-assertion that it is at once convincing and impressive.

These investigators were subsequently attached to the University of Cracow, and much of their work dates from that city. The results are published in various languages. There is no need to study Polish to read them.

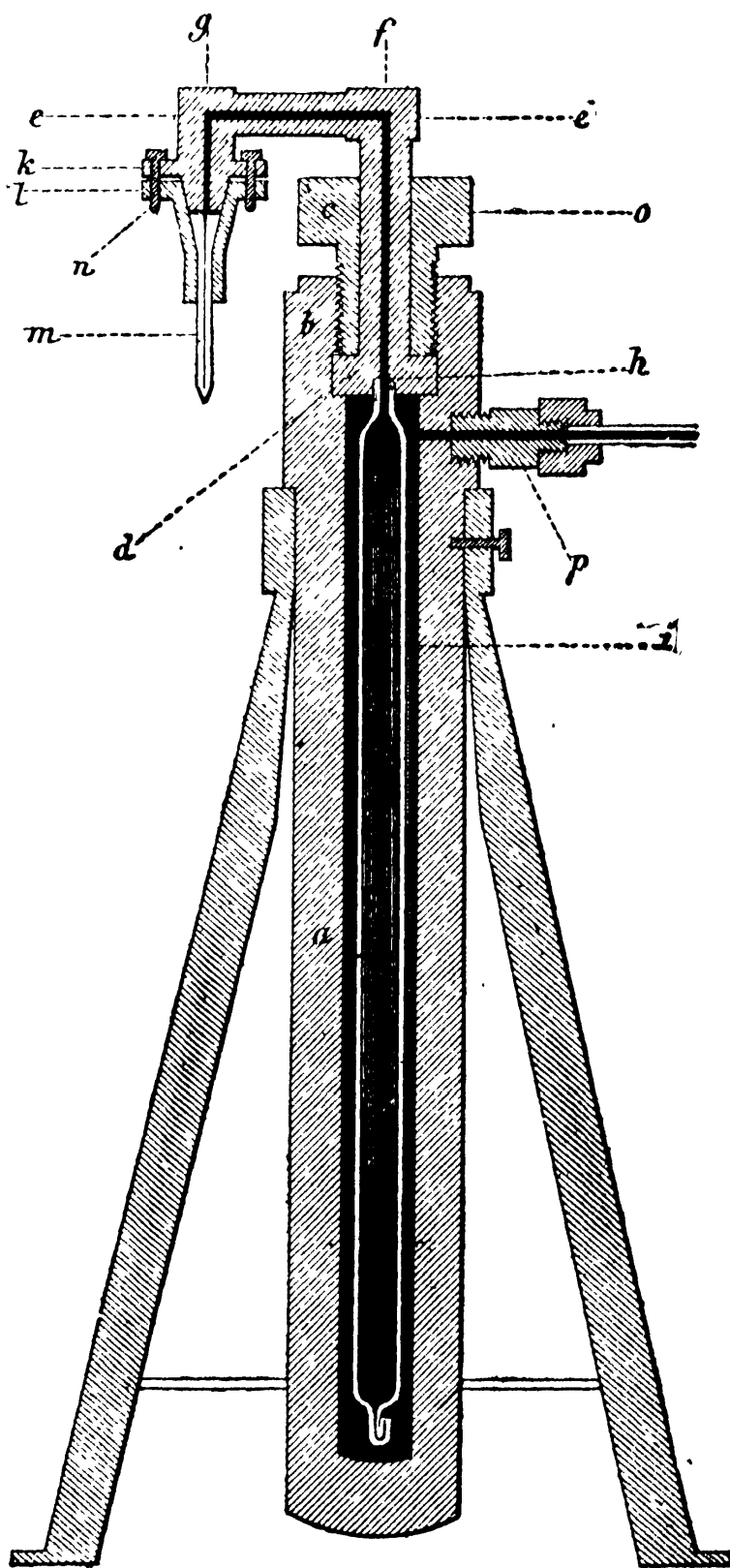
"One of us," Wroblewski, while in Paris studied Cailletet's apparatus and methods, and had an apparatus made by a Paris mechanic, E. Ducretet, for the prosecution of researches on liquefied gases. The point is made that it is superior to the Cailletet apparatus of that early date because it could be used with five or six times as much gas as could be used in Cailletet's apparatus.

The apparatus may be considered in two divisions—one the condensing apparatus by which the gas to be experimented on was subjected to pressure, the other the refrigerating apparatus for cooling it below the critical temperature.

We reproduce the cuts of the apparatus from *Wiedemann's Annalen*. It will be seen that the gas compression apparatus is practically a copy of Cailletet's apparatus, so that the apparatus goes back to

the days of Colladon. In the gas refrigerating portion will be found a reminder of Pictet's circuits, not as yet fully utilized by the Polish scientists.

The gas tube, *z*, is designed to hold about 200 cubic centimeters of gas. It has an upturned capillary tube at its bottom. A very thick-walled capillary tube extends from its top and bends downward. The cylinder, *a*, which contains the gas tube, is of heavy cast iron. Very exact dimensions are given in the paper in *Wiedemann's Annalen* already cited. The general dimensions are stated as 58



Wroblewski and Olszewski's Gas Compression Vessel.

centimeters (23.2 inches) deep and 8.5 centimeters (3.4 inches) wide.  $c$  and  $o$  is a bronze piece which forms a tight connection between the gas tube,  $i$ , and the upper tube,  $e, f, g, e$ . A very strong steel tube runs through the orifice in the piece,  $d$ . To get it in place the horizontal portion of the piece in question was sawed through horizontally in the line,  $e, c$ , and bored downward from  $g$  and  $f$ . The steel tube was inserted in place, a groove along the line,  $e, e$ , receiving it. The piece which was sawed off was replaced and brazed in its former place, so as to surround the steel tube.

At the end,  $h$ , the steel tube expands, and the glass gas tube,  $i$ , is cemented into it. At  $k$  the bronze steel-lined piece has a conical end.  $m$  is a glass tube cemented in place, and all is secured by a coned piece,  $l$ , with screws,  $n$ , as shown, the screws uniting all parts to an airtight joint.

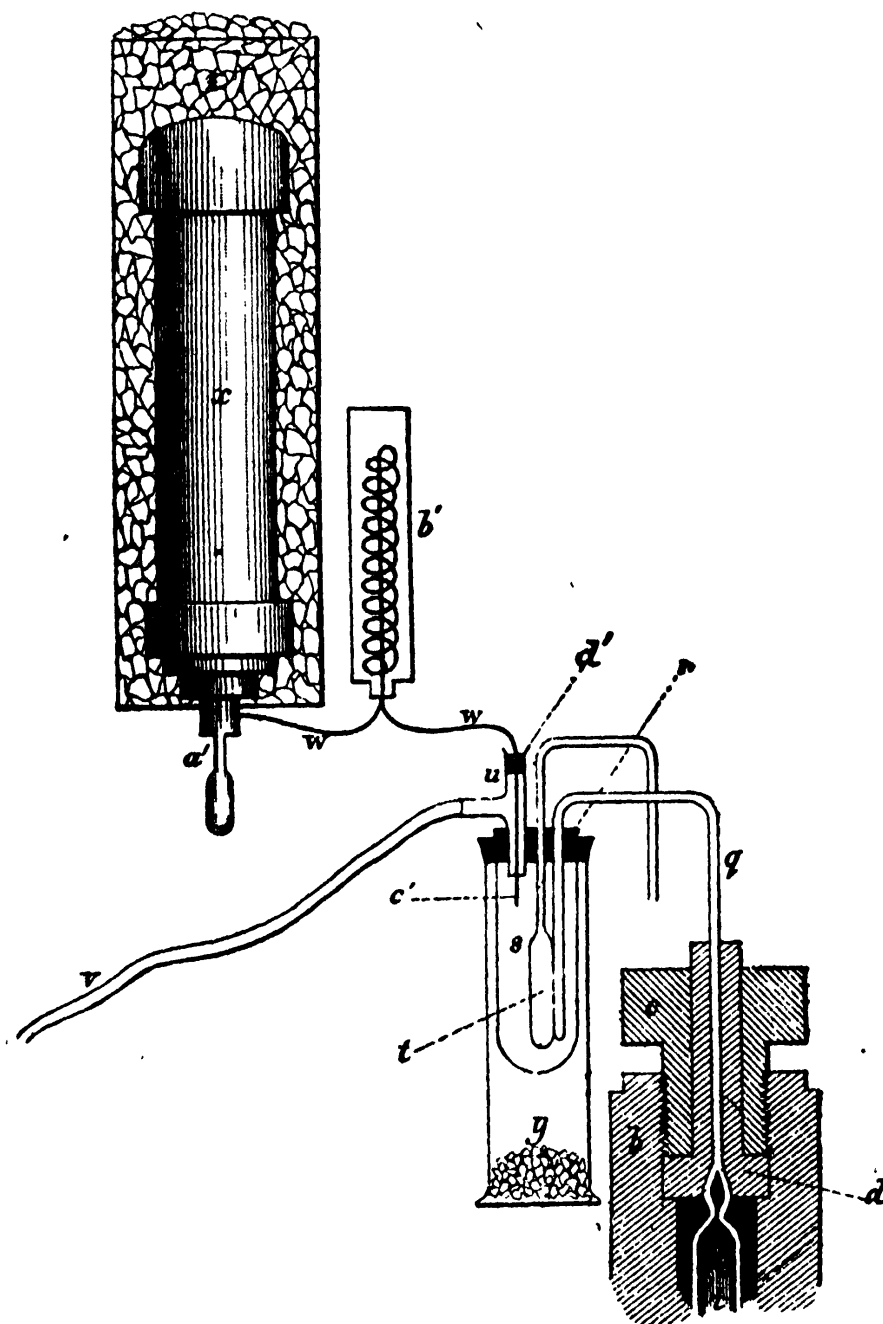
At  $p$  a tube is connected which leads to a force pump.

The next illustration shows how the apparatus was set up for the liquefying of gases in the downwardly extending tube from the compressing apparatus. This cut is also an exact reproduction of the cut given in *Wiedemann's Annalen*.

We have, as before, the vessel,  $i$ , with its steel containing vessel,  $b$ , only the top of which is shown. The capillary tube,  $q$ , was 0.9 centimeter (0.36 inch) external diameter and a little over 0.2 centimeter (0.08 inch) internal diameter. The glass vessel,  $i$ , was filled with the gas to be experimented with.

A jar,  $y$ , has calcium chloride at its bottom to keep the air within it perfectly dry. A second vessel,  $s$ ,

is set into it airtight with an india rubber stopper. The vessel, *s*, is provided with an india rubber stopper of its own, perforated for three tubes. One is



Wroblewski and Olszewski's Apparatus for Liquefying Gases.

the end, *q*, of the gas tube, *i*, the other the stem of the hydrogen thermometer, *t*. The third receives a T shaped tube, *u*. Liquid ethylenc is contained in the



cylinder, *x*, where it is kept cool with ice and salt. The liquid ethylene is withdrawn at *a*, through a thin tube, *w*. This tube is coiled into a cooler, *b'*, charged with liquid and solid carbon dioxide. This brings it down to a very low temperature.

As needed it is drawn into the vessel, *s*. An air pump connected to the T tube, *u*, by the tube, *v*, produces an almost full vacuum in the vessel, *s*. The upper end of the T tube is provided with an india rubber cork through which the tube, *w*, passes airtight, the liquid ethylene dropping from *c*.

The gas to be experimented on was introduced into the tube, *i*, mercury was contained in the vessel, *b*, and the pressure was increased to any desired extent by pumping water into *b*. The end of the gas tube, which was sealed and bent down, was cooled by admission of the cooled ethylene into the vessel, *s*, and this vessel was pumped out by an air pump, so that it was kept down to a pressure of but  $2\frac{1}{2}$  millimeters of mercury, which is a small fraction of an atmosphere. The ethylene, when first admitted to the vessel, *s*, boiled tumultuously, but soon quieted down and kept slowly boiling, thereby producing a very low temperature.

Each experiment required 200 to 300 grammes of ethylene and about 400 grammes of solid carbon dioxide. Very little ethylene was lost.

The apparatus worked well. The only trouble chronicled was due to the mercury freezing in the capillary tube, which brought about an explosion which did no great injury.

The temperatures were taken by the hydrogen thermometer, *t*, whose bulb, it will be observed, is

placed in the refrigerating vessel, not in the gas experimented with. Thus the temperature recorded is that of the environment of the sample, not that of the sample itself, which is a defect worthy of comment.

While on the subject of thermometers, it may be noted that there occurs in the *Wiedemann's Annalen* article an interesting statement to the effect that Natterer told "one of us," orally, that he filled his low temperature thermometer with phosphorus chloride. This gives us a glance at the work of a preceding generation and is mentioned elsewhere in this book.

The results obtained with this apparatus were very good. Oxygen liquefied at  $-130^{\circ}$  C. ( $-202^{\circ}$  F.) and at a pressure of a little over 20 atmospheres. It was a colorless fluid, the slight blue tint not showing, presumably because of its slight amount. It had a flatter meniscus than that of carbon dioxide. On reducing the pressure to a relatively small degree it foamed, evaporated from the surface, and on further reduction, boiled throughout its entire mass.

The work of these investigators at about this period is the subject of other papers in the *Comptes Rendus* and elsewhere.

In the *Comptes Rendus*, vol. xcvi., is given the dispatch announcing Wroblewski's liquefaction of oxygen. It was received by M. Debray, secretary of the Academy of Sciences, on April 9, 1883, from Cracow. It reads as follows:

"Oxygène liquéfié, complètement liquide, incolore comme l'acide carbonique. Vous recevrez une note dans quelques jours."

“Oxygen liquefied, completely liquid, colorless like carbonic acid. You will receive a note in a few days.”

The “note” which follows is given in the same volume of the *Comptes Rendus* and alludes to Cailletet’s ethylene paper (*ibid.*, vol. xciv., page 1224). The authors say that Cailletet did not fully satisfy himself. Wroblewski and Olszewski, with apparatus made by “one of us” (“*un de nous*”), who was in this case Wroblewski, and using a quantity of oxygen, effected the liquefaction. They found liquid oxygen colorless and transparent, very mobile, and giving a sharp meniscus.

With boiling ethylene in approximate vacuum they got a temperature of  $-136^{\circ}$  C. ( $-212.8^{\circ}$  F.) by the hydrogen thermometer. They found that at the atmospheric pressure ethylene boils at  $-102^{\circ}$  to  $-103^{\circ}$  C. ( $-151.6^{\circ}$  to  $153.4^{\circ}$  F.), and not at  $-105^{\circ}$  C. ( $-157^{\circ}$  F.) The following data for oxygen were determined on April 9:

At temperature of  $-131.6^{\circ}$  C. ( $-204.9^{\circ}$  F.) begins to liquefy at 25.5 atmospheres.

At temperature of  $-133.4^{\circ}$  C. ( $-208.1^{\circ}$  F.) begins to liquefy at 24.8 atmospheres.

At temperature of  $-135.8^{\circ}$  C. ( $-212.4^{\circ}$  F.) begins to liquefy at 22.5 atmospheres.

They took advantage of their ethylene apparatus to try some other experiments in the direction of freezing carbon bisulphide and alcohol.

Carbon bisulphide froze at about  $-116^{\circ}$  C. ( $-176.8^{\circ}$  F.), alcohol became thick like sirup at about  $-129^{\circ}$  C. ( $-200.2^{\circ}$  F.), and froze a degree lower,  $-130^{\circ}$  C. ( $-202^{\circ}$  F.)

On April 16, 1883, another dispatch was received by the secretary of the Academy of Sciences, telling of the same investigators' liquefaction of nitrogen:

“Azote refroidi, liquéfiée par détente. Menisque visible, liquide incolore.”

“Nitrogen cooled, liquefied by release. Visible meniscus, colorless liquid.”

The note which gives the details of the liquefaction of nitrogen says that they exposed nitrogen at  $-136^{\circ}$  C. ( $-212.8^{\circ}$  F.) to a pressure of 150 atmospheres. On sudden release there was a tumultuous ebullition (“*aufbrausen*”) like that of carbon dioxide in a Natterer's glass tube of carbon dioxide (page 23) when it is plunged into water which is a little warmer than the critical temperature of carbon dioxide. Then they tried a partial release from pressure, lowering it to 50 atmospheres, when the nitrogen liquefied completely with a meniscus. It remained a few seconds only. It was colorless and transparent.

On April 21, 1883, the following dispatch was received by the Academy from the same investigators:

“Oxyde de carbone liquéfié dans les mêmes conditions que l'azote. Ménisque visible. Liquide incolore.”

“Carbon monoxide liquefied under the same conditions as nitrogen. Meniscus visible. Colorless liquid.”

Hydrogen they failed to liquefy. It was cooled to  $-136^{\circ}$  C. ( $-212.8^{\circ}$  F.), compressed to 150 atmospheres, then was suddenly released, but not even a mist appeared. Boiling oxygen is recommended as

a cooling agent, but the impetuosity with which it boiled was a great obstacle to its use. Even at one atmosphere of pressure it proved uncontrollable. The duration of its ebullition was very short, and this proved an objection. Eight years later, in 1891, Olszewski overcame this trouble by bubbling hydrogen through it gradually. Cailletet's production of cold by bubbling a gas through a volatile liquid, as described on page 201, may be noted also. By a thermo-electric couple its temperature was determined. It is given as  $-186^{\circ}$  C. ( $-302.8^{\circ}$  F.)

Nitrogen was compressed and cooled with boiling oxygen without result, but on sudden release from pressure it formed snow-like crystals of remarkable size.

In 1883 Wroblewski and Olszewski attacked the problem of determining the specific gravity of pure oxygen. They introduced a known quantity of oxygen into their apparatus and liquefied it as completely as possible. This gave them an approximation, if they neglected to take into account the unliquefied gas which lay above the liquid. To determine what value this unliquefied portion had, a control experiment was done with liquid carbon dioxide whose specific gravity was known, the experimenters using Andréeff's determination (*Liebig's Annalen*, vol. cx., page 1). The calculations are too complicated to be here reproduced. The result obtained for oxygen at about  $-130^{\circ}$  C. ( $-202^{\circ}$  F.) and the pressure of liquefaction was 0.899.

Wroblewski, still longing to produce liquid oxygen in quantity, says, in December, 1883, that it is merely a question of appliances to produce liquid

oxygen, but acknowledges that he has never succeeded in producing oxygen in the condition of a static liquid. Any attempt to use the refrigerating effect of oxygen, he said, involves its use at the instant of production or cessation of pressure. Such danger of explosion attended attempts in this direction that masks were worn.

A valuable suggestion would seem to be the one made in 1884, when Wroblewski suggests the use of liquid marsh gas as a refrigerant. In its properties it is adapted to fill the gap which exists between liquid ethylene and liquid oxygen. The honor of being the first in the field with this suggestion was afterward claimed by Cailletet. Dewar, however, was able to show that he had suggested the use of liquid marsh gas as far back as 1883, which antedates Wroblewski, and Cailletet's date goes back to 1881.

After this period the two scientists appear as individual workers. The path started on the lines of Cailletet's and Pictet's work led to direct experimental determinations, but these appear in later work. The early apparatus, just described, did not lend itself to thoroughly reliable temperature observations. Indirect methods of dealing with problems had to be used, and in some cases data were reached on almost purely theoretical grounds. This was done to some extent quite recently, and the hydrogen data were determined with fair approximation partly from a theoretical basis.

Much ingenuity appears in the methods of attacking the problems which presented themselves in the course of their experimentation. As an example

may be cited the determination of the critical temperature and pressure of oxygen (*Comptes Rendus*, vol. xcvi.)

Oxygen gas was liquefied in the downwardly bent tube, *q*, of the apparatus, page 209, by the aid of boiling ethylene contained in the vessel, *s*, as already described. As the oxygen liquefied its level rose in the tube, *q*, and eventually reached a point above the level of the liquid ethylene in *s*. Now it is evident that, as the liquid oxygen reaches a point in the gas tube above the ethylene, the temperature of its upper layers is higher, and the more it rises, the higher is this temperature. As the temperature increases, the pressure necessarily rises.

At last a point is reached when evidences of the critical state begin to show themselves. The meniscus flattens, the line of demarkation between liquid and gas becomes indistinct and at last entirely disappears. The only way to trace the position of any separating level is by the difference of refractive power of the different layers in the tube. The description as given by Wroblewski exactly describes the phenomena observed in a Natterer's tube (page 23).

If the pressure is lowered, the temperature of the oxygen falls, liquefaction ensues, and the meniscus again forms. Working in conjunction with Olszewski, the investigator found that this phenomenon of the critical state occurred always at about the pressure of 50 atmospheres.

The pressure of oxygen under these conditions is so high and its temperature so low that it appeared desirable to exercise some sort of a check upon this

experiment. The same tube was charged with liquid carbon dioxide overlaid by the gas, in exact analogue with the conditions of the oxygen experiment. The boiling ethylene was replaced by melting ice, and warm water at  $50^{\circ}$  C. ( $122^{\circ}$  F.) surrounded the upper part of the tube. Hence, within the length of the gas tube the temperature had a range of  $50^{\circ}$  C.

Pressure was applied, and at 35 atmospheres traces of liquid carbon dioxide appeared in the bottom of the tube, which was the cold part. The gas kept on liquefying until the liquid rose above the level of the melting ice and began to reach the warm portion of the gas tube. The pressure increased as the liquefied carbon dioxide attained in its upper layers a higher temperature.

As the pressure approached 76 atmospheres the meniscus became flat, then indistinct, and eventually disappeared. The critical state was reached. On lowering the pressure, the liquid diminished in amount, the level fell, and the upper layer reached a cooler part of the tube. The meniscus at once showed itself again. The appearance and disappearance of the meniscus evidently took place at a point of the tube where the critical temperature existed. The pressure in the apparatus when the phenomena described took place was the critical pressure.

The attempt was made now to ascertain the critical temperature of oxygen—a far more difficult factor to determine. A small quantity of oxygen was liquefied in the apparatus, so that it was below the level of the liquid ethylene. The latter was boiling under exhaustion so as to give a very low degree of temperature. The exhaustion was stopped and the



temperature of the ethylene began to rise. The meniscus was watched.

Two things were occurring in the tube. The temperature was rising and the pressure increasing as the ethylene became warmer. Sooner or later the balancing point, the critical state, would be reached and the disappearance of the meniscus gave the indication. This was watched for, the temperature of the ethylene being constantly observed.

The observations were extremely difficult, and Wroblewski gives the figure of  $-113^{\circ}$  C. ( $-171.4^{\circ}$  F.) in his own words, "as the first approximation to the critical temperature of oxygen." The temperature we now know was too high by nearly  $6^{\circ}$  C.

Cailletet had brought before the French Academy of Sciences his liquefaction of hydrogen (page 184). He had on release from pressure obtained a mist or fog, which he claimed was due to liquid hydrogen. Naturally some doubt was felt about it.

Wroblewski had tried it, and in an early number of the *Comptes Rendus*—early as regards its date—referring to the history of the liquefaction of oxygen and of the "permanent gases," says that he tried Cailletet's experiment and failed.

On January 4, 1884, the following dispatch from Wroblewski was received by the French Academy of Sciences:

"Hydrogène refroidi par oxygène bouillant s'est liquéfié par détente."

"Hydrogen cooled by boiling oxygen has been liquefied by release."

Debray commented on the dispatch and says that this experiment confirms Cailletet's experiment.

In the *Comptes Rendus* of February, 1884, Wroblewski tells of his liquefaction of hydrogen. He compressed hydrogen to 100 atmospheres in a glass tube whose general dimensions were from 0.2 cm. to 0.4 cm. (0.08 inch to 0.16 inch) in internal diameter and 2 cm. (0.8 inch) external diameter. It was arranged for very sudden release of pressure. The tube was surrounded with boiling oxygen in order to reduce the temperature of the hydrogen. On sudden release of pressure the hydrogen gave the mist as in Cailletet's experiment of 1882.

To determine the temperature a thermocouple was used, which was connected to a galvanometer which could show a potential difference of  $\frac{1}{400000}$  volt, which corresponded to half a degree on the thermometric scale. It was standardized by comparison with a hydrogen thermometer.

It was known that the electric resistance of metals falls with the reduction of temperature. As early as 1835 Wroblewski had tried silk-covered copper wire, cooled to a temperature of  $-200^{\circ}$  C. ( $-328^{\circ}$  F.), and found that its resistance was less than one-hundredth of what it was at the temperature of boiling water. He says that oxygen and nitrogen, in the liquid state, are among the most perfect insulators known. He says that the electric resistance of copper, at a temperature approaching that of boiling nitrogen, tends to become zero—the conductivity approaches perfection.

This view has been very prominently brought forward again by Dewar and others, and Elihu Thomson goes so far as to believe that in liquid gases a useful reducer of electric resistance for power dis-

tribution may be found. It is certainly very captivating to think of a thin copper wire in a pipe filled with liquid air carrying the energy of Niagara Falls over hundreds of miles of country.

An experiment which excited much comment, and which now, in these days of wholesale liquefaction of air, is almost lost sight of, was described by Wroblewski, who, in 1885, in liquefying air, produced from it two liquids superimposed and which remained separate for some minutes. He managed to withdraw, by a metallic tube, samples from each layer for analysis—rather a delicate operation, it would seem. On analysis, the lower layer, after gasification, gave a little over one-fifth of its volume of oxygen (21.28 per cent. to 21.5 per cent. oxygen). The upper liquid gave a little over seventeen-hundredths of its volume of oxygen after gasification (17.3 per cent. of nitrogen).

Wroblewski had used various thermometers for determining the low temperatures which he obtained in his experiments, the hydrogen-filled thermometer seeming eventually to give him most satisfaction. Cailletet had used various thermometers, finally tending to the hydrogen one. Pictet had adopted a very indirect method of calculating temperatures, and the thermo-couple had also been employed, as we have just seen.

In 1885 Wroblewski published a paper embodying his experiments on the relations existing between temperatures as determined by the hydrogen thermometer and a thermo-electric couple of copper and German silver.

After this year but little appears under the name of

this distinguished investigator. He seemed to possess the rare faculty of not disputing with any of his confrères. The disputes as to priority in the liquefaction of gases are very numerous and extend over the greater part of a century. Wroblewski was fortunate in not being involved in any of them, as far as his own statements are concerned at least.

Wroblewski and Olszewski worked together for a number of years, but the latter scientist continued the same line of work alone up to a recent period. In the *Philosophical Magazine*, March, 1895, he published a *résumé* of his work, incidentally giving vent to a certain amount of feeling and attacking Dewar and Pictet.

In 1885 Olszewski made what may be called an approximate liquefaction of hydrogen. He mixed two volumes of hydrogen with one volume of oxygen and liquefied the mixture successfully. The mixture was colorless. On release from pressure it lost most of its hydrogen. The residual liquid lasted for some time at the atmospheric pressure.

He is much interested in showing that he produced oxygen in quantity large enough to pour from one vessel into another. In October, 1890, he produced 100 cubic centimeters before an audience, and in July of the succeeding year, also before an audience, he produced 200 cubic centimeters. He lays great stress on this achievement.

His apparatus, by which he produced oxygen in what were large quantities for the period, was very simple. Its essential feature was the use of a steel cylinder of small capacity in which the oxygen was

liquefied. This took the place of the glass tube in which the gases were liquefied in the original Wroblewski and Olszewski experiments.

In 1883 and the subsequent years the two associated investigators had liquefied gases in glass tubes. The almost capillary tube of their early experiments was changed sometimes for a larger one. Thus the following are given as the dimensions of a tube in which many liquefactions were carried out: The tube was 30 centimeters (about 12 inches) long and 14 to 18 millimeters (0.56 to 0.72 inch) in internal diameter. The walls were 3 to 4 millimeters (0.12 to 0.16 inch) thick.

All the "permanent" gases then known, from which argon, helium and the companions of argon must be excluded, for they were not yet discovered, had been liquefied in this apparatus, as already described, and nitrogen, carbonic oxide, nitric oxide and marsh gas had been solidified.

It will be observed, especially if the cut of the 1883 apparatus (page 209) be inspected, that no means were provided for drawing off the small amount of liquefied gas which might be produced in the glass tube. If an attempt had been made to substitute a large glass bulb for the tube, it would never have stood the strains due to changes of temperature and high pressure. By the repetition of numberless liquefactions, the conditions necessary to produce them became so accurately known that it was no longer necessary to see the liquefaction to know that it was produced. The necessity for a transparent vessel had ceased.

Olszewski accordingly substituted for the glass

tube a small steel reservoir. This would stand the pressure without danger of explosion, and was so good a conductor of heat that the most sudden changes of temperature had not the least effect upon it in the direction of causing it to break.

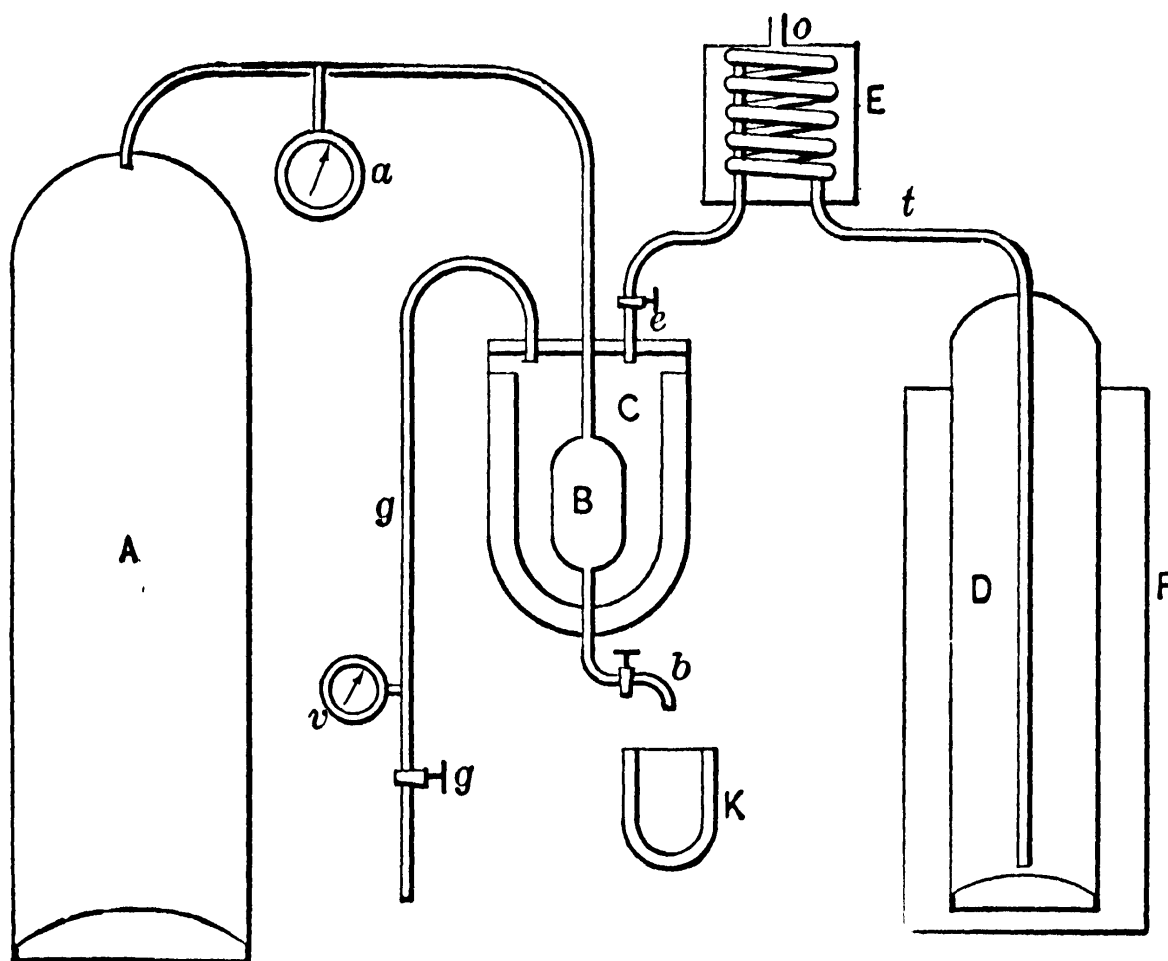
This apparatus was described in 1890 in the *Bulletin internationale de l'Academie de Cracovie*. While Olszewski, in the *Philosophical Magazine* article, seems to indicate that his work has not been fully enough appreciated, he makes very evident one reason. He gives the list of his original papers. So many of them appeared in the *Cracow Bulletin*, whose title is given above, that they were deprived of the circulation which was their due and which would have been secured by a wider publication in the German, French and English scientific annals.

But Olszewski's steel reservoir, like Pictet's liquefaction tube, was provided with a cock by which its contents could be withdrawn, and this certainly was an advance over a sealed glass tube. The probabilities are that in 1883 the possibility of handling liquid gases at atmospheric pressure like so much water was undreamed of.

The mechanically bad feature of Pictet's old apparatus was present in this one, which comes some thirteen years later. The liquid was drawn from a reservoir in which it was confined under enormous pressure. The outrush of the almost uncontrollable fluid must have given some trouble to the experimenter.

We give the diagram of the steel reservoir apparatus with which oxygen was liquefied in quantities sufficient to pour from one vessel into another.

*A* is a cylinder of oxygen gas compressed to 100 atmospheres. It is connected by a tube to the steel reservoir, *B*. From the lower end of the steel reservoir a tube with stopcock, *b*, descends. A gauge, *a*, indicates the pressure of the oxygen. It is obvious that any considerable diminution of pressure would indicate liquefaction.



Olszewski's Liquefaction Apparatus of 1890.

The reservoir, *B*, is contained in a double-walled vessel, *C*, hermetically closed at the top. From it one tube, *g*, runs to an exhausting pump. This tube has a cock, *g*, and vacuum gauge, *v*. Another tube, *t*, runs to an ethylene cylinder, *D*. This tube has a stopcock, *e*, and is bent into a coil between *C* and *D*.

The coil is contained in a vessel, *E*, which is charged with a mixture of ether and solid carbon dioxide. A tube, *o*, leads from this vessel, which is absolutely tight, to an exhausting pump. *D* contains liquid ethylene, which is kept cold by ice and salt mixture in the outer vessel, *F*.

The oxygen under high pressure filled the steel vessel, *B*, which was quite small, of but a few ounces capacity. Here it was subjected to the refrigeration due to the liquid ethylene, cooled by exhausted carbon dioxide and ether, and also subjected to exhaustion, so as to have its temperature greatly reduced by boiling. The intense cold, which was below the critical temperature of oxygen, rapidly liquefied it under pressure, and soon the vessel, *B*, filled with the liquid. It could then be drawn off by opening the cock, *b*.

By opening and shutting the cocks the apparatus could be manipulated very readily, and the pressure gauge, *a*, and vacuum gauge, *v*, gave certain indications of the progress of operations. If the apparatus is analyzed and reduced to its elements, it will be seen to be a simplification of Pictet's apparatus of 1877, simplified by the suppression of pump circuits and by the use of compressed gases. It will be seen to be much the same as Dewar's apparatus of 1883 (page 236), and the latter expresses himself as of the opinion that the substitution of the steel reservoir for the glass tube which he employed was not a very important change.

To keep this delivery under some control, the outlet tube from the steel oxygen vessel had lateral openings. This prevented the stream of liquid from



rushing out against the bottom of the vessel and driving out the contents as fast as received.

It is impossible within the limits of this work to give the entire work of any investigator. Olszewski determined many constants, by many methods, and the general abstract of his work, with table of constants determined and bibliography or list of his papers, may be found in the *Philosophical Magazine* for 1895.

For determining low temperatures he used as a matter of preference the hydrogen thermometer, and used it to standardize a platinum resistance thermometer when the temperature fell too low for the hydrogen instrument. But he distrusts all except the hydrogen thermometer, except under limited and defined conditions. Extrapolation he naturally suspects, and, on account of variations in specific heat as lower temperatures are reached, he has little confidence in calorimeter methods.

During his investigations he was troubled with bursting tubes. His work, like that of other investigators, was not of the safest order.

James Clerk Maxwell, one of the most illustrious physicists and mathematicians of England, had doubted the possibility of liquefying hydrogen. Faraday had not felt so. He believed that it might yet be accomplished, and expresses himself in rather uncertain phrase concerning it. Olszewski had no hopes of liquefying it in volume or as "static hydrogen." The lesson of Cailletet's production of cold by release from pressure seems to have been lost to the world, only to be successfully applied within the last five years by Tripler, Linde, Hampson and

Dewar. But without attempting to liquefy it in large volume, Olszewski tried to determine the constants of liquid hydrogen. Now, his temperatures ran so low that he was forced to use a platinum resistance thermometer, which he compared with a hydrogen thermometer, with the following result:

Temperature by hydrogen thermometer.	Electrical resistance of platinum resistance thermometer.
0° C. (32° F.).....	1000 ohms.
—78.2° C. (—108.8° F.).....	800 “
—182.5° C. (—296.5° F.).....	523 “
—208.5° C. (—343.3° F.).....	453 “

This shows the decrease in electrical resistance due to reduction of temperature which is utilized as a thermometric factor. But more is shown. The fall in electrical resistance per degree fall in temperature grows greater as the temperature descends. Thus:

	Ohms.
Between 0° and —78.2° C. the fall per degree is	2.557
“ —78.2° “ —182.5° C. “ “ “ “	2.655
“ —182.5° “ —208.5° C. “ “ “ “	2.692

The last figure was adopted for the extrapolation, or carrying out the scale beyond the limits of the experiment.

He found for hydrogen a critical temperature of —234.5° C. (—390.1° F.) and a boiling point at atmospheric pressure of —243.5° C. (—406.3° F.) The lowest static temperature Olszewski claims to have attained is —225° C. (—373° F.) The hydrogen temperatures were of exceedingly brief duration.

The method adopted for reaching this figure de-

pended on the observation that if a gas is exposed to high pressure and is then cooled to a temperature not far from the critical temperature, a slow reduction of pressure will bring about liquefaction of the gas. The appearance of a mist indicated the liquefaction. The result of numerous experiments with hydrogen showed that this mist appeared always at exactly the same pressure if the experimenter started with a high enough pressure.

Thus he varied the initial pressure all the way from 80 to 140 atmospheres by 10 atmospheres at a time, cooled the compressed gas to  $-211^{\circ}$  C. ( $-347.8^{\circ}$  F.) and suffered the gas to expand, watching the change in pressure as it did so, and watching for the mist. This mist always showed itself at 20 atmospheres of pressure, whether the initial pressure was high or low, provided it did not range below 80 atmospheres.

If the initial pressure did fall below this point then the pressure at which liquefaction took place also fell, and, starting from initial pressure of 50, 60 and 70 atmospheres, the mist appeared at pressures of 14, 16 and 18 atmospheres respectively. All constancy was lost.

Therefore, Olszewski accepted 20 atmospheres as the critical pressure of hydrogen, and thence deduced the conclusion that hydrogen liquefying at 20 atmospheres had the critical temperature. As he could always produce the slight evidences of liquefaction at this pressure in the small glass tube, he believed that he could always produce liquid hydrogen at the critical temperature by establishing the conditions described.

The only trouble was that such a minute quantity of hydrogen was liquefied in his glass tube that it was impossible to determine its temperature. He, therefore, resorted to his steel vessel apparatus (page 224), established the proper conditions of initial pressure and temperature, slowly reduced the pressure to 20 atmospheres, and took the temperature of the hydrogen in the steel vessel.

He saw no liquefaction, for the steel vessel hid its contents. He established the conditions which had always produced the mist in the transparent glass tube, and he relied upon the large size of the steel vessel to give enough liquid hydrogen to affect the electric resistance thermometer which he employed.

Dewar, after producing liquid hydrogen in quantity so that it could be poured from vessel to vessel, and so that its temperature could be accurately determined, comments unfavorably on Olszewski doing his work in an opaque vessel. Although, too, Olszewski's assumptions seem rather forced, and led him to too high a critical pressure figure, his results are surprisingly good, and compare well with Wroblewski's calculated ones and Dewar's presumably more accurate ones.