

SCIENCE

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LIQUID OXYGEN.

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It is now fifteen years since Pictet and Cailletet first liquefied oxygen. Since then liquid oxygen has been the object of investigation by Olsewski, Wroblewski, and more particularly by Dewar. At a lecture delivered at the Royal Institution in London, in June last, Dewar exhibited a litre of liquid oxygen in an open vessel; and he has prepared from time to time many litres of the liquid for the purpose of examining its properties. The method he uses is the same in principle as Pictet's, but he has much larger and better pumps for exhausting and compressing the gases. The essential thing is to cool the oxygen well below its critical temperature, or absolute boiling point, -119°C . This is effected by means of some other gas, such as ethylene, which has a much higher critical temperature, namely $+10^{\circ}\text{C}$., and still a very low boiling point under atmospheric pressure, namely -103° . Nitrous oxide, which has a critical temperature of $+53^{\circ}\text{C}$., and boils under atmospheric pressure at -93°C ., may also be employed. If the liquid ethylene be first cooled to -80°C . by immersion in a mixture of solid carbonic acid and ether, it can then be easily reduced to -103° by allowing it to evaporate at the pressure of the air; and by pumping away the vapor as fast as formed the temperature of the remaining liquid can be reduced as low as -140° , twenty-one degrees below the critical temperature of oxygen. At this temperature oxygen is liquid if condensed until its pressure is equal to 30 atmospheres or thereabouts. On removing the pressure the liquid boils and is cooled by its own evaporation until under a pressure of one atmosphere it falls to -183°C . By pumping away the gas as it is formed, the temperature is easily reduced to -200°C ., and the liquid then remains quite tranquil, and has the appearance of so much water.

Air may be liquefied in the same way, but the boiling point of nitrogen is somewhat lower than that of oxygen, namely -193°C ., so that when liquid air is allowed to boil away gradually, the residue becomes richer and richer in oxygen until nearly pure liquid oxygen is left.

The compressed oxygen met with in commerce always contains a little air and some carbonic acid, and both pass into the liquid oxygen. The carbonic acid crystallizes out in the solid state and renders the liquid milky. It may, however, be filtered through paper, and is then perfectly limpid.

To prevent the rapid deposition of hoar frost on the vessel containing the cold liquid, it has to be protected by an outward vessel, and the intervening space well dried. A beaker glass may be fitted with a varnished wooden cover and a smaller beaker to contain the liquid inserted through a hole in the cover, the space between the two being dried by a layer of phosphoric anhydride.

Oxygen does not show any increased chemical activity in consequence of liquefaction. As already mentioned it may be filtered through paper without affecting the paper. It is powerfully magnetic. Poured into a saucer of rock salt it at once assumes the spheroidal state, exaporating from its surface, but quite tranquil. If now it be brought near the pole of an electro-magnet, it will jump up, through half an inch or more, and adhere to the pole, looking like a blob of transparent ice. Of course it is not really solid, and as soon as the current of the electro-magnet is broken it falls down. Like iron it is attracted by either pole indifferently.

As it is the only transparent element which is magnetic, its behavior to light is of great interest with reference to the electro-

magnetic theory of light. According to that theory it would be expected that light reflected from a plane surface of a transparent magnetic body, when the reflected and transmitted rays are at right angles, would not be polarized in the plane of incidence as it is when the reflecting body is diamagnetic. Dewar has found, however, that light incident at the proper angle and reflected by liquid oxygen at -200°C . is very completely polarized in the plane of incidence.

Seen by transmitted light liquid oxygen, in a thickness of three or more inches, has a faint, but decided, blue tint. On examining the transmitted light through a prism, the cause is plain. There are several absorption bands, of which the strongest is in the yellow. These bands, as observed by Olsewski, and by Liveing and Dewar who extended their observations into the ultra-violet, are identical in position with, but much darker than, the diffuse bands produced by oxygen gas. They coincide with certain diffuse dark bands noticed by Brewster in the solar spectrum, and ascribed by him to atmospheric absorption because they were stronger when the sun was near the horizon than when he was high in the sky. The persistence of these bands indicates continuity in the physical state of oxygen when passing from the gaseous to the liquid state.

It was observed by Jannsen, and Liveing and Dewar's observations tend to the same conclusion, that the intensity of these diffuse bands, for a given thickness of the gas, increases as the square of the density. On the kinetic theory such a result would follow if the molecules of oxygen absorb the corresponding rays when they are under the influence of other molecules but not when in free path. For both the number of the molecules in a given thickness, and the frequency of their collisions, increase directly as the density.

Furthermore, oxygen gas produces, besides these diffuse bands, certain absorptions consisting of rhythmical groups of fine lines. These, in the solar spectrum, are known as *A*, *B*, and α ; and it was Egoroff who identified these lines with the absorptions of oxygen gas. Their intensities appear to increase directly as the density, and may therefore fairly be ascribed to the action of the free molecules of oxygen gas. What becomes of these absorptions when the gas is liquefied? Olsewski, looking through 30 millimeters of the liquid, observed an absorption at the place of *A*. Liveing and Dewar, looking through six inches of the liquid, saw absorptions corresponding to both *A* and *B*, but somewhat different from those due to the gas. As produced by the gas, *A* is a group of lines which are very close together on the less refrangible side and are set farther and farther apart as they get more refrangible; so that the group when seen with low dispersion has the appearance of a shaded band with a strong, sharp edge on the less refrangible side, gradually fading away on the more refrangible side. *B* is on the blue side of *A*, and is precisely similar to it, but not so intense. α is still more refrangible, and still weaker. The absorption of the liquid at the place of *A* is also a shaded band, but its shading is turned the other way. Its sharp and strongest edge is on its more refrangible side, and it fades away on the less refrangible side. The strong edge does not correspond exactly with the strong edge of *A*, but is a little more refrangible, though still falling within the group. The band of the liquid could not be resolved, like *A*, into lines. The band corresponding to *B* is precisely similar, but fainter. It overlaps *B*, and has its strong edge a little more refrangible than that of *B*. It seems that we have in these bands the absorptions due to the individual molecules of oxygen, only modified in the way described by the change from gas to liquid; and we should infer that the molecules of the liquid are still the same as those of the gas.

There is more difficulty in determining the physical characters of oxygen than the facility with which it can be manipulated

would lead one to expect. It is especially difficult to find suitable vessels for it. Thin glass in one piece, like test-tubes and beakers, does very well, but thick glass and all kinds of cement are mostly cracked by cooling; and massive vessels involve the waste of a large volume of the liquid in the process of cooling them down to -180°C . With some trouble, however, Liveing and Dewar have succeeded in measuring the refractive index of liquid oxygen, at its boiling point, for the D ray of sodium. They used a hollow prism with glass faces clamped together and made tight at the joints with glycerine. The refractive index so found was 1.2236, somewhat less than that of water in the liquid state, which, near its boiling point, is about 1.32.

The density of oxygen at -182° is 1.124. These figures give for the refraction constant, $\frac{\mu^2 - 1}{(\mu^2 + 2)d} = .1265$, and for the corresponding refraction equivalent 2.024. The mean values of the constant and equivalent as found by Mascart and Lorenz for gaseous oxygen are the same as those here given for the liquid.

Ozone is more easily liquefied than ordinary oxygen, but is formed with a storage of energy, and in a concentrated state is very explosive. When oxygen, ozonized in a Siemens' tube cooled with solid carbonic acid and ether, is passed into liquid oxygen, the ozone is dissolved and imparts a deep-blue color to the liquid. The boiling point of oxygen is lower than that of ozone, so that, as the oxygen evaporates, the strength of the solution and the depth of its color increase. The last drop has a steel-blue color, and explodes spontaneously with violence. If a glass tube conveying ozonized oxygen be cooled down to -180°C , or nearly so, the liquid ozone may be seen condensing on the sides and running down. It has been found impossible to collect the liquid, however, for no sooner have two or three small drops run together than they explode, shattering the vessel.

It is certainly remarkable that a substance which, unlike many substances which are formed with a storage of energy, is so unstable at high temperatures, should also be very unstable at low temperatures. Perhaps its instability may be connected with its powerful absorption of light, which is put in evidence by its deep color. What the form may be in which its excessive energy is stored, we can at present only guess at. Can it be that the three atoms, of which its molecule consists, rotate with great velocity about their common centre of mass in exceeding close proximity, and that a small impulse from without increasing the velocity as well as the distance of the atoms suffices to send them off in hyperbolic orbits to scatter destruction amongst the other molecules which they encounter? This might be the case if the velocity of the atoms greatly exceeds the velocity of agitation of the molecules on which the temperature depends.

NEW DISCOVERIES AT BAOUSSÉ ROUSSÉ, NEAR MENTONE.

BY THE MARQUIS DE NADAILLAY.

I KNOW of no discovery touching pre-historic times more remarkable than those made in the caves of Baoussé Roussé, between Mentone and Ventimiglia, on the borders of France and Italy. These caves were first discovered in 1872 by Mr. Rivière. Since that time this learned gentleman has vigorously prosecuted his excavations,¹ and they have yielded numerous human skeletons, all belonging to the celebrated Cro-Magnon race, who at the end of the quaternary period, or perhaps at the beginning of neolithic times, ruled not only the south of France, but also all the Mediterranean shores. It is these same men we meet with under the names of Iberians, Ligurians, Sicanians, perhaps also under those of Pelasgians and Berbers. It is their bones that the brothers Siret found in the south of Spain, Professor Sergi in Italy, and Mr. Rivière at Baoussé Roussé.

All the bones, wherever found, show a great similitude. They are robust, and bespeak an athletic constitution and a large muscular power. The men were remarkably tall, the crania are dolichocephalic, the tibias platynemic, but since Dr. Manouvrier's

¹ They are related at length in "L'Antiquité de l'homme dans les Alpes maritimes." Paris, I. B. Baillière et fils, 1887.

observations,² we cannot see there an inferior character. The cranium of the first skeleton found (an old man) measured 1,590 cubic centimeters. The cranium of the woman found next to him 1,450 cubic centimeters; but this last measurement is not quite accurate, on account of the decomposed state of the bones.

The man had upon his head a net of small shells (*Nassa neritea*), and bracelets of shells round his arms and legs. Near him Mr. Rivière collected more than 150 stone implements, and also numerous bones of mammals, birds, and fishes, evidently the food of these people.

New discoveries quickly followed the first ones, and we always find a particular mode of inhumation, which, I believe, still exists, or lately existed, in some Indian tribes. The bones of all the adults, after the total decomposition of the flesh, were painted in red with the help of peroxide of manganese or other substances frequently met with in the different caverns.

The last excavations took place in February, 1892, in one of these caves, named Barma Grande. A communication made to the Académie des Inscriptions, March 4, 1892, informed us of the discovery, at 8 metres below the level of the ground, of three new skeletons, a man, a woman, and a young subject whose denticulæ had not yet evolved. They had been buried on a bed of cinders, broken fragments of charcoal, remains of all sorts, evidently the hearth on which the family cooked their victuals. The boy wore a necklace formed of two rows of the vertebrae of a fish and one row of small shells. At different points hung pendants cut out of the canine teeth of stags, decorated with parallel striæ. The man had also a necklace of fourteen canines of the stag, also striated. With the skeletons were found a certain number of stone instruments, some of them finely worked, but none of them polished, and some bone implements of very gross fabrication.

The man was very tall, and, if we judge by the length of the thigh-bone (545 millimeters), his height must have exceeded two metres³ (6 feet 6 inches). The boy, who had not yet attained his manhood, measured 1.63 metres (5 feet 8 inches). We must also remark the extreme wear of the teeth, very apparent already in the boy, and which in the man extended to their very root. I have already said that the caves of Baoussé Roussé yielded numerous bones of mammals, but none of them belonged to the extinct species, not even to the reindeer which is found in the south of France even at a late period. On the other hand, no polished stone implement was ever found in these caves. We can therefore give these men a pretty accurate date, and place their existence, as I have said, at the end of the quaternary or the beginning of the neolithic times. One cave remains as yet unexcavated. It belongs to the Prince of Monaco. Orders are given that the excavations shall begin next spring. If they produce anything of interest, I will not fail to report them to the readers of *Science*.

Rougemont, Sept. 2.

THE PREVENTION OF CHOLERA ASIATICA.

BY HUGH HAMILTON, M.S.C., M.D.

THE symptoms of cholera are so well known that it is a matter of common knowledge; however, to make the subject plain, it is very similar to *Cholera Morbus*, well known to every American, which is due to indigestion and disorder from the eating of improper fruits or too large amounts of perfect raw fruit. In *Cholera Asiatica* there is vomiting, purging, chill, sweat, death in a longer or shorter period. When *Cholera Asiatica* is epidemic, many of these lesser complaints of the digestive apparatus pass under its name, and, as a consequence, many remedies seem to cure the disease, which in fact is probably not *Cholera Asiatica* but *Cholera Morbus*, which is bad enough.

² Dr. Manouvrier has shown that platynemia is produced by long and hard work continuously acting on the muscles of the leg. It is found to a large extent in hard walkers, in populations living near the mountains. It is more frequent in men than in women; and it very rarely, if ever, exists in children.

³ The state of the bones precluded any accurate measurement, and comparison, when we reach these extreme heights, is very difficult. The Museum of Paris possesses the skeleton of a giant who measured 2.14 metres, and whose thigh-bone measured 563 millimeters.