

"The Absorption and Thermal Evolution of Gases occluded in Charcoal at Low Temperatures." By Sir JAMES DEWAR, M.A., D.Sc., LL.D., F.R.S., Jacksonian Professor, University of Cambridge, and Fullerian Professor, Royal Institution, London. Received June 15,—Read June 16, 1904.

During the year 1874—5, in association with the late Professor Tait, a research was undertaken which involved the production of very perfect vacua, and with the object of improving on the then known methods, dense charcoal was employed as an efficient absorbent of traces of any gaseous residuum.

An account of these experiments communicated to the Royal Society of Edinburgh appeared in 'Nature,' July 15, 1875, under the title of "Charcoal Vacua."

In Professor Clerk Maxwell's Notes on "Molecular Physics" the following succinct description of the process is given:—

"Another method employed by Professor Dewar is to place in a compartment of the vessel a piece of freshly heated cocoanut charcoal, and to heat it strongly during the last stages of the exhaustion by the mercury pump. The vessel is then sealed up, and as the charcoal cools it absorbs a very large proportion of the gases remaining in the vessel.

"The interior of the vessel, after exhaustion, is found to be possessed of very remarkable properties.

"One of these properties furnishes a convenient test of the completeness of the exhaustion. The vessel is provided with two metallic electrodes, the ends of which within the vessel are within a quarter of an inch of each other. When the vessel contains air at the ordinary pressure a considerable electromotive force is required to produce an electric discharge across this interval. As the exhaustion proceeds, the resistance to the discharge diminishes till the pressure is reduced to that of about a millimetre of mercury. When, however, the exhaustion is made very perfect the discharge cannot be made to take place between the electrodes within the vessel, and the spark actually passes through several inches of air outside the vessel before it will leap the small interval in the empty vessel. A vacuum, therefore, is a stronger insulator of electricity than any other medium."

At one of the conferences held in connection with the Special Loan Collection of Scientific Apparatus* in the year 1876, I showed that with a vapour like bromine the absorptive power of the charcoal was so effective that a space filled with the vapour even at atmospheric pressure could be made into a fairly high vacuum showing very wide striæ.

* See 'Science Conferences,' "Physics and Mechanics," p. 154.

When the charcoal was heated the bromine vapour was again expelled, and on allowing it to cool, all stages in the appearance of the electric discharge as the vacuum is reached could be conveniently observed without the use of any form of air-pump.

When in the course of low temperature investigations the perfection of the vacuum vessels for the storage and manipulation of liquid air and hydrogen came to be important, the effect of charcoal on heat isolation in such utensils was fully investigated and confirmed in a paper entitled "*Liquid Air as an Analytic Agent.*"* Still no systematic experiments on the absorptive power of charcoal at low temperatures were made either at this time or subsequently.

It is the object of the present preliminary paper to contribute some definite quantitative data regarding gas absorption and thermal evolution in charcoal at the temperature of liquid air. The mode in which liquid gases like oxygen or air could be used as calorimetric agents was described in my paper on the "*Scientific Uses of Liquid Air.*"†

The apparatus was further improved into the form illustrated and described in Madame Curie's Work, "*Recherches sur les Substances Radio Actives,*" 2nd edition, p. 100, as used for the determination of the heat evolved by radium bromide either in liquid oxygen or hydrogen. Such calorimeters are easily adapted to the simultaneous observation of the volume of any gas absorbed by charcoal, and of the concomitant heat evolution.

For this purpose a small glass bulb C containing from 0·5—1 gramme of charcoal has a long narrow tube C attached, so that it can be immersed in the liquid oxygen or air in the calorimeter A B, while still allowing a part of the tube to project above the cork A. In order to dry and cool the 40 c.c. of gas, which represents the largest volume taken in by the charcoal in my experiments, a little annular space is arranged at D into which liquid air is poured immediately before the experiment is made.

The charcoal, after being placed in the tube C, is heated to a low red heat and simultaneously exhausted by a good air-pump, and after all the gas has been removed the stop-cock E is closed. In this condition it is placed in the calorimeter.

The experiment is conducted by connecting the end of the tube at E by means of an india-rubber tube with a graduated vessel F containing the gas. When all is ready the stop-cock E is opened, so that the gas may rush into the charcoal, and the heat evolved by its absorption distils off the equivalent quantity of liquid air from the calorimeter, which is measured in the vessel G.

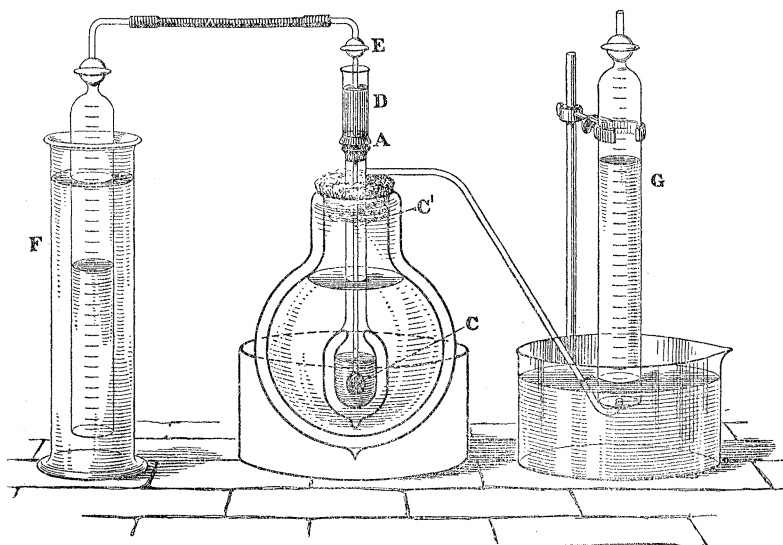
The constant of the calorimeter being known (which with liquid air

* '*Roy. Inst. Proc.,*' 1898.

† '*Roy. Inst. Proc.,*' 1894.

is about 14·5 c.c. per calorie), we get the actual thermal evolution together with the volume of gas absorbed.

The heat correction for the rush of gas into the same exhausted glass bulb without charcoal is small in proportion to the total heat evolved, and the same may be said of the volume correction on account



of the cooling of the space external to the charcoal. With a variable material like cocoanut charcoal I have in the calorimetric experiments used the same sample in all cases. The following table embodies the general results per cubic centimetre of charcoal. The gas absorption is given at 0° and 760 mm. If the volume of gas absorbed had been measured under the same conditions of pressure at -185° C., then the numbers in Column II would all have to be divided by three.

	I. Volume absorbed. 0° C.	II. Volume absorbed. -185° C.	III. Heat evolved. Gramme calories.
Hydrogen	4 c.c.	135 c.c.	9·3
Nitrogen.....	15 „	155 „	25·5
Oxygen	18 „	230 „	34·0
Argon	12 „	175 „	25·0
Helium	2 „	15 „	2·0
Electrolytic gas	12 „	150 „	17·0
Carbonic oxide and oxygen	30 „	195 „	34·5
Carbonic oxide	21 „	190 „	27·5

In all cases, it will be observed, the amount of gas occluded has been greatly increased at the low temperature, and the degree of condensation is generally such as we should anticipate from the known physical constants of the gases. The amount of heat evolved is so great as to be in excess of that required for liquefaction in the case of gases like hydrogen, nitrogen, and oxygen. The heat produced when successive fractions of the volume of gas required for saturation are absorbed has yet to be determined. In the time required for the absorption no measurable amount of chemical combination was effected between mixtures of hydrogen and oxygen or carbonic oxide and oxygen in the pores of the charcoal.

Such experiments must be extended to the use of platinised charcoal and other catalytic agents.

Perhaps the most striking result is the great difference in properties exhibited by helium. While resembling the other gases in showing increased absorption at the temperature of liquid air, the absolute amount occluded per unit volume of charcoal is about one-tenth that of the other gases at the same temperature. There can be little doubt that when the relative absorption of helium in charcoal is measured at the temperature of liquid hydrogen, the increased absorption will be so marked as to make it comparable to that of hydrogen in the present set of experiments. In this case charcoal at the boiling point of hydrogen will become an efficient condensing agent for helium, and this property will have important applications in future research.

Separation of Highly Concentrated Oxygen from Air.

In order to examine the changes taking place in a mixed gas like air during the absorption, a quantity of about 50 grammes of charcoal was after heating and exhaustion saturated at -185° in a current of pure dry air; got by passing the air current through a U-tube immersed in liquid air.

For a time the air rushed into the charcoal with great rapidity, and in about 10 minutes between 5 and 6 litres were taken in. A manometer attached to the vessel containing the charcoal showed, on shutting off the air current, that during the early part of the saturation the absorption was so effective as to give practically no measurable mercury pressure. As soon as the absorption was ended, and a current began to pass slowly over the charcoal, the composition of the air leaving the charcoal showed 98 per cent. nitrogen. After the current of air had passed for half an hour, the total gas occluded in the charcoal was expelled by taking the vessel in which it had been treated out of the liquid air, and allowing the temperature to rise to 15° C.

The gas, which was rapidly expelled, measured 5.7 litres, and contained 56 per cent. of oxygen. If the saturated charcoal before

heating up was subjected for an hour to the action of an air-pump, capable of giving a steady exhaustion of 5 mm., no difference was effected in the oxygen percentage of the evolved gas. The same experiment was repeated with this variation, that, instead of the air current having the pressure of the atmosphere, it was kept below one-tenth of an atmosphere. In this experiment, 4·8 litres were expelled on heating up, and the percentage of oxygen was 58. Then, a further repetition was made with an air current supplied at a pressure not exceeding 5 mm. of mercury. After 3 hours' treatment, the charcoal, on heating to 15° C., gave 4½ litres of 57 per cent. oxygen. From these experiments it follows that the tension of the occluded gases, at the temperature of liquid air, must be very small, and thus the use of low temperatures, combined with charcoal, introduces a new and greatly improved means of getting high vacua, which in the future may be found susceptible of important practical applications. These experiments are quite conclusive as to the practical constancy of the mean composition of the air gases occluded in the charcoal (subject to the conditions aforesaid), and they further show that wide changes in the pressure of the air current has little or no effect in altering the proportions. In another experiment, the vessel containing the saturated charcoal, instead of being allowed to rise rapidly in temperature, was transferred to a vacuum vessel, in which a little liquid air was placed, in order that the temperature might rise slowly, and thereby enable the successive litres of gas given off to be collected separately and analysed.

This experiment gave the following results :—

	Oxygen per cent.
First litre	18·5
Second „	30·6
Third „	53·0
Fourth „	72·0
Fifth „	79·0
Sixth „	84·0

The mean composition of the 6 litres is again 56 per cent. oxygen. From the above experiments it follows that one of the most rapid means of extracting a high percentage of oxygen from atmospheric air is to absorb it in charcoal at low temperatures, and then to expel it either rapidly or slowly by heating the mass of charcoal to the ordinary temperature.

A few experiments have been made using, instead of air, special mixtures of oxygen and nitrogen. Thus it was found that a gas containing 6·5 per cent. of oxygen used in the same manner as in the air occlusion experiments, gave, on heating up the charcoal rapidly to 15° C., 5 litres of gas having the composition of 23 per cent. of oxygen.

A repetition of the same process with the 23 per cent. of oxygen would have raised the percentage about 60 per cent., or a stronger concentration could have been reached by fractionating the gas as it slowly leaves the charcoal on gradually increasing the temperature.

This preliminary investigation suggests many fields for further inquiry, and some of these I hope to deal with in future papers.

I have to express my thanks to Mr. Robert Lemox, F.C.S., for efficient aid in the conduct of the experiments, and Mr. J. W. Heath, F.C.S., has also rendered valuable assistance.

“The Separation of the most Volatile Gases from Air without Liquefaction.” By Sir JAMES DEWAR, M.A., D.Sc., LL.D., F.R.S., Jacksonian Professor, University of Cambridge, and Fullerian Professor, Royal Institution, London. Received June 15,—Read June 16, 1904.

From the time when liquid air came to be an ordinary laboratory agent, I have continually used it for the purpose of producing high vacuum vessels that had been previously filled with easily condensable gases, such as sulphurous acid, carbonic acid, vapour of water or benzol.

When the liquefaction of hydrogen was effected one of the first scientific uses to which it was put was that described in my paper on the “Application of Liquid Hydrogen to the Production of High Vacua, together with their Spectroscopic Examination.”* In that communication it was shown by theory and confirmed by experiment that the condensing power of liquid hydrogen is so great relatively to that of liquid oxygen or nitrogen, that any closed vessel, a part of which is cooled to the boiling point of hydrogen must suddenly become a highly vacuumous space. This was proved by the great difficulty of getting electric discharges to pass through specially prepared spectroscopic tubes when subjected to liquid hydrogen cooling, and from the fact that when the current did pass no lines of oxygen or nitrogen were seen, but only those of hydrogen, helium and neon. In order to separate these latter gases from air it was necessary to liquefy a quantity of air and to distil off the most volatile portion at as low a temperature as possible into a separate receiver placed in liquid hydrogen. In this way many spectroscopic tubes were filled with the uncondensable air gases and the results of their examination is recorded in a paper entitled “On the Spectra of the more Volatile Gases of Atmospheric Air, which are not Condensed at the Temperature of Liquid Hydrogen,”† by Professor Liveing and myself.

* ‘Roy. Soc. Proc.’ vol. 64, 1898.

† ‘Roy. Soc. Proc.’ vol. 67, 1900.

