THE CONTINUITY OF THE GASEOUS AND LIQUID STATES OF MATTER*

It may be truly affirmed of Physical Science, that its history, for some generations at least, has been one of rapid progress and unceasing change, and that its most earnest promoters have not claimed infallibility for their opinions, nor finality for their results. Its advancing progress has been marked by eras when some long-accepted theory or hypothesis, which had appeared so closely in accordance with all known experiments and observations as to have been received as an obvious truth, has, by further experiments extending into regions previously unexplored, been found to be a faulty or incomplete representation of the phenomena.

Such an era has occurred in the discovery recently announced by Dr. Andrews of the Continuity of the Gaseous and Liquid States of Matter.

We have all been accustomed to consider matter as existing in one or other of three states,—the solid, liquid, and gaseous.

Fig. 1.

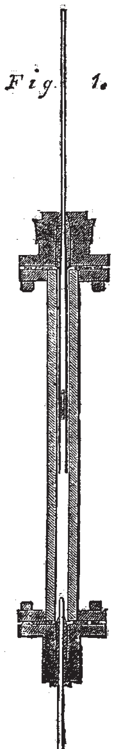
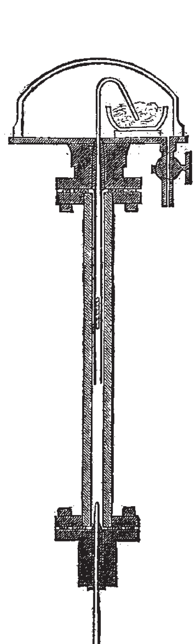


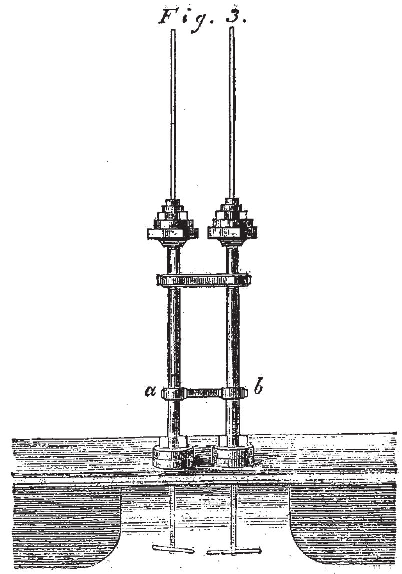
Fig. 2.



The transition, from any one of these states to another, has hitherto been regarded as necessarily abrupt; at least, if we except the imperfectly understood conditions of softening or plasticity, assumed by such bodies as glass or iron, when gradually passing from the solid to the molten condition. The true state of the case is now found to be very different.

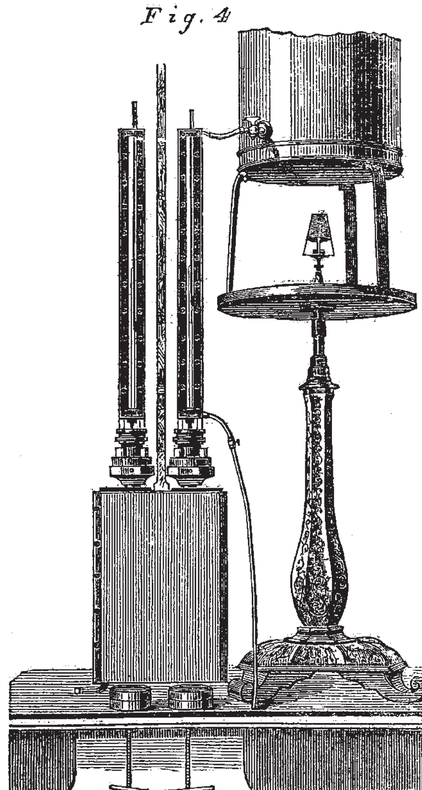
The memoir of Dr. Andrews, of which we propose to give an account in this article, opens with the following historical *résumé* of previous researches bearing more or less in the direction of his investigations:—"In 1822 M. Cagniard de la Tour observed that certain liquids, such as ether, alcohol, and water, when heated in hermetically sealed glass tubes, became apparently reduced to vapour in a space from twice to four times the original volume of the liquid. He also made a few numerical determinations of the pressures exerted in these experiments. In the following year Faraday succeeded in liquefying, by the aid of pressure alone, chlorine and several other bodies known before only in the gaseous form. A few years later Thilorier obtained solid carbonic acid, and observed that the coefficient of expansion of the liquid for heat is greater than that of any aëriform body. A second memoir by Faraday, published in 1845, greatly extended our knowledge of the effects of cold and pressure on gases. Regnault has examined with care the absolute change of volume in a few gases when exposed to a pressure of twenty atmospheres,

Fig. 3.



and Pouillet has made some observations on the same subject. The experiments of Natterer have carried this inquiry to the enormous pressure of 2,790 atmospheres; and although his method is not altogether free from objection, the results he

Fig. 4



obtained are valuable, and deserve more attention than they have hitherto received."

In 1861 a brief notice appeared of some early experiments by Dr. Andrews in this direction. Oxygen, hydrogen, nitrogen,

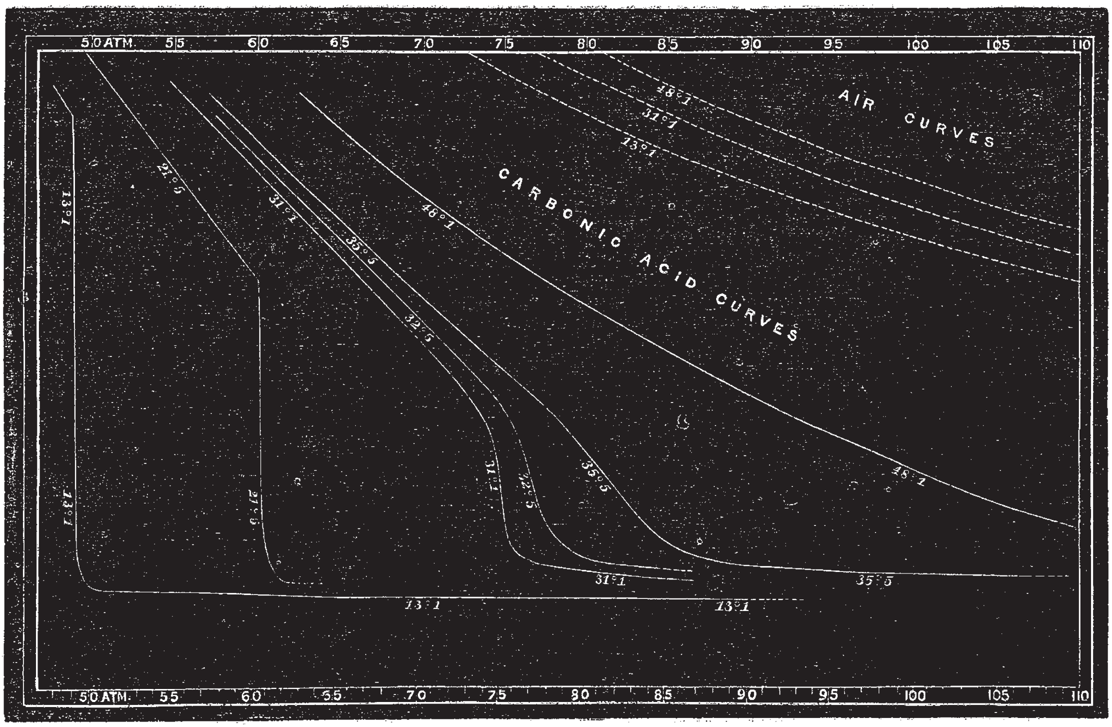
* "The Bakerian Lecture for 1869." By Thomas Andrews, M.D., F.R.S. (Abridged from an Original Essay of Professor James Thomson, LL.D.)

carbonic oxide, and nitric oxide were submitted to greater pressures than had previously been attained in glass tubes, and while under these pressures they were exposed to the cold of the carbonic acid and ether bath. None of these gases exhibited any appearance of liquefaction, although reduced to less than $\frac{1}{500}$ of their ordinary volume by the combined action of cold and pressure. Subsequently, in the third edition of Miller's "Chemical Physics," published in 1863, a short account, communicated by Dr. Andrews, appeared of some further results he had obtained, under certain fixed conditions of pressure and temperature, with carbonic acid. These results constitute the foundation of the researches which form the general subject of the present article, and the following extract from the original communication of Dr. Andrews to Dr. Miller may here be quoted:—"On partially liquefying carbonic acid by pressure alone, and gradually raising at the same time the temperature to 88° Fahr., the surface of demarcation between the liquid and the gas became fainter, lost its curvature, and at last disappeared. The space was then occupied by a homogeneous fluid, which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout its entire mass. At temperatures above 88°, no apparent liquefaction of carbonic acid or separation into two distinct forms of matter could be effected, even when a pressure of 300 or 400 atmospheres was applied. Nitrous oxide gave analogous results."

For his recent researches Dr. Andrews again selected carbonic acid as the substance for investigation. He devised for his experiments an apparatus, novel in construction, and well suited to exhibit the properties acquired by fluids under very varied conditions of pressure and temperature. The carbonic acid was contained in a glass tube, capillary in the upper and larger part of its length, and for the remainder, of the widest bore in which a column of mercury would remain without displacement when the tube was placed in a vertical position. A movable column or bar of mercury confined the gas to be operated on. This glass tube was secured by careful packing in a massive end-piece of brass, which carried a flange, by means of which a water-tight junction could be made with a corresponding flange, attached to a cold-drawn copper tube of great strength. To the other end of the copper tube a similar end-piece was firmly bolted. The latter carried a fine steel screw, 7 inches long, which was packed with such care that the packing was capable of resisting a pressure of 400 atmospheres or more. A section, exhibiting all the details, is given in Fig. 1. Before commencing an experiment the body of the apparatus was filled with water; the upper end-piece, carrying the glass tube, in which was the gas to be operated on, was firmly secured in its place, and the pressure was obtained by screwing the steel screw into the water chamber. In Fig. 2 the same apparatus is shown with the modifications required when the gas or liquid is exposed to very low temperatures under high pressure. The end of the capillary tube dips into a bath of ether and solid carbonic acid, under a bell jar, from which the air may be exhausted.

In order to estimate the pressure exerted in these experiments, a duplex or compound form of the apparatus was employed, as shown in Fig. 3. The two sides of the apparatus freely communicate through *a b*, so that on turning either of the steel screws the pressure is immediately transmitted through the entire apparatus. In the second tube a known volume of air is confined, and the pressure is approximately estimated by its contraction.

Figure 4 exhibits the complete apparatus with the arrangements for maintaining the capillary tubes and the body of the apparatus itself at fixed temperatures. A rectangular brass case, closed before and behind with plate glass, surrounds each capillary tube, and allows it to be maintained at any required temperature by the flow of a stream of water. In the figure, the arrangement for obtaining a current of heated water in the case of the carbonic-acid tube is shown. The body of the apparatus itself, as is shown in the figure, is enclosed in an external vessel of copper, which is filled with water at the temperature of the apartment. This latter arrangement is essential when accurate observations are made.



The temperature of the water surrounding the air-tube was made to coincide, as closely as possible, with that of the apartment, while the temperature of the water surrounding the carbonic-acid tube varied in different experiments from 13° C. to 48° C. In the experiments as they were performed, the mercury did not come into view in the capillary part of the air-tube till the pressure amounted to about forty atmospheres. The volumes of the air and of the carbonic acid were carefully read by a cathetometer, and the results could be relied on with certainty to less than 1-20 of a millimetre or 1-500 of an inch. We must refer the reader to the original memoir for an account of the details of the experiments, and of the numerous precautions adopted to secure accuracy. The object of the present article is to place as clearly as possible before his mind the main results arrived at, and the general features of the apparatus employed.

In the above diagram, we have a graphical representation of the results of a large number of comparative experiments on air and carbonic acid, under pressures ranging from 48 to 107 atmospheres, and at temperatures for the carbonic acid varying from 13°·1 C. to 48°·1 C. The dotted lines (*Air Curves*) represent a portion of the curves of a perfect gas (assumed to have the same volume originally at 0° C., and under one atmosphere as the carbonic acid), for the temperatures of 13°·1 C., 31°·1 C., and 48°·1 C. The lines designated *Carbonic Acid Curves* show the volumes to which the carbonic acid is reduced at the temperatures marked on each curve, and under the approximate pressures indicated by the numbers at the top and bottom of the figure. Ordinates drawn from the inner horizontal line at the lower part of the figure to meet the curves, will represent the volume of the carbonic acid. These ordinates do not always refer to homogeneous matter, but sometimes to a mixture of gas and liquid.

It will be observed that in the curves for 13°·1 C. there occurs an abrupt, or almost quite abrupt, fall, when a pressure of about 49 atmospheres has been attained. The curve for 21°·5 C. exhibits a corresponding fall, but not till a higher pressure (about 60 atmospheres) has been reached. On close inspection of the figure, a slight deviation from perfect abruptness will be observed in the portion of the curves representing these falls, which Dr. Andrews showed to be due to a trace of air (about $\frac{1}{500}$ part) in the carbonic acid with which the experiments were made. Had the carbonic acid been absolutely pure, there can be no doubt that the fall would have been quite abrupt.

In the curve for 31°·1 C. there is no abrupt fall; but a rapid descent, indicating a corresponding diminution of volume, occurs between the pressures of 73 and 75 atmospheres. As the temperature rises this descent becomes gradually less marked, and when a temperature of 48°·1 C. has been attained, it has almost, if not altogether, disappeared.

At any temperature between −57°C., and 30°·92 C., carbonic acid, under the ordinary pressure of the atmosphere, is unquestionably in the state of a gas or vapour. If within these limits we take a given volume of carbonic acid, and gradually augment the pressure, the volume will steadily diminish, not however uniformly, but according to a more rapid rate than the law for a perfect gas, till we reach the point at which liquefaction begins. A sudden fall or diminution of volume will now take place, and with a little care it will be found easy so to arrange the experiment that part of the carbonic acid shall be in the liquid, and part of it in the gaseous state; the carbonic acid thus coexisting in two distinct physical conditions in the same tube, and under the same external pressure. But if the experiment be made at 30°·92 C., or any higher temperature, the result will be very different. At 30°·92 C., and under a pressure of about 74 atmospheres, the densities of liquid and gaseous carbonic acid, as well as all their other physical properties, become absolutely identical, and the most careful observation fails to discover any heterogeneity at this or higher temperatures in carbonic acid, when its volume is so reduced as to occupy a space in which, at lower temperatures, a mixture of gas and liquid would have been formed. In other words, all distinctions of state have disappeared, and the carbonic acid has become one homogeneous fluid, which cannot by change of pressure be separated into two distinct physical conditions. This temperature of 30°·92 is called by Dr. Andrews the *critical point* of carbonic acid. Other fluids which can be obtained in both the liquid and gaseous states have shown similar phenomena, and have each presented a critical point of temperature. The rapid changes of density which slight changes of temperature or pressure produce, when the gas is reduced at temperatures a little above the critical point, to the volume at which it might be expected to liquefy, account for the flickering movements referred to in the beginning of this article.

The general conclusions arrived at we give in the words of the original memoir. "I have frequently exposed carbonic acid," observes Dr. Andrews, "without making precise measurements, to much higher pressures than any marked in the tables, and have made it pass, without break or interruption, from what is regarded by every one as the gaseous state, to what is, in like manner, universally regarded as the liquid state. Take, for example, a given volume of carbonic acid gas at 50° C., or at a higher temperature, and expose it to increasing pressure till 150 atmospheres have been reached. In this process its volume will steadily diminish as the pressure augments, and no sudden diminution of volume, without the application of external pressure, will occur at any stage of it. When the full pressure has been applied, let the temperature be allowed to fall, till the carbonic acid has reached the ordinary temperature of the atmosphere. During the whole of this operation, no breach of continuity has occurred. It begins with a gas, and by series of gradual changes, presenting nowhere any abrupt alteration of volume or sudden evolution of heat, it ends with a liquid. The closest observation fails to discover anywhere indications of a change of condition in the carbonic acid, or evidence, at any period of the process, of part of it being in one physical state and part in another. That the gas has actually changed into a liquid would, indeed, never have been suspected, had it not shown itself to be so changed by entering into ebullition on the removal of the pressure. For convenience this process has been divided into two stages, the compression of the carbonic acid, and its subsequent cooling; but these operations might have been performed simultaneously, if care were taken so to arrange the application of the pressure and the rate of cooling that the pressure should not be less than 76 atmospheres when the carbonic acid had cooled to 31°.

"We are now prepared for the consideration of the following important question. What is the condition of carbonic acid when it passes, at temperatures above 31°, from the gaseous state down to the volume of the liquid, without giving evidence at any part of the process of liquefaction having occurred? Does it continue in the gaseous state, or does it liquefy, or have we to deal with a new condition of matter? If the experiment were made at 100°, or at a higher temperature, when all indications of a fall had disappeared, the probable answer which would be given to this question is that the gas preserves its gaseous condition during the compression; and few would hesitate to declare this statement to be true, if the pressure, as in Natterer's experiments, were applied to such gases as hydrogen or nitrogen. On the other hand, when the experiment is made with carbonic acid at temperatures a little above 31°, the great fall which occurs at one period of the process would lead to the conjecture that liquefaction had actually taken place, although optical tests carefully applied failed at any time to discover the presence of a liquid in contact with a gas. But against this view it may be urged, with great force, that the fact of additional pressure being always required for a further diminution of volume, is opposed to the known laws which hold in the change of bodies from the gaseous to the liquid state. Besides, the higher the temperature at which the gas is compressed, the less the fall becomes, and at last it disappears.

"The answer to the foregoing question, according to what appears to me to be the true interpretation of the experiments already described, is to be found in the close and intimate relations which subsist between the gaseous and liquid states of matter. The ordinary gaseous and ordinary liquid states are, in short, only widely separated forms of the same condition of matter, and may be made to pass into one another by a series of gradations so gentle that the passage shall nowhere present any interruption or breach of continuity. From carbonic acid as a perfect gas to carbonic acid as a perfect liquid, the transition we have seen, may be accomplished by a continuous process, and the gas and liquid are only distant stages of a long series of continuous physical changes. Under certain conditions of temperature and pressure, carbonic acid finds itself, it is true, in what may be described as a state of instability, and suddenly passes, with the evolution of heat, and without the application of additional pressure or change of temperature, to the volume which by the continuous process can only be reached through a long and circuitous route. In the abrupt change which here occurs, a marked difference is exhibited, while the process is going on, in the optical and other physical properties of the carbonic acid which has collapsed into the smaller volume, and of the carbonic acid not yet altered. There is no difficulty here, therefore, in distinguishing between the liquid and the gas. But in other cases the distinction cannot be made; and under many of the conditions I have described it would be vain to attempt to assign carbonic acid to the liquid rather than the gaseous state. Carbonic acid, at the temperature of 35°·5, and under a pressure of 108 atmospheres, is reduced to $\frac{1}{430}$ of the volume it occupied under a pressure of one atmosphere; but if any one ask whether it is now in the gaseous or liquid state, the question does not, I believe, admit of a positive reply. Carbonic acid at 35°·5, and under 108 atmospheres of pressure, stands nearly midway between the gas and the liquid; and we have no valid grounds for assigning it to the one form of matter any more than to the other. The same observation would apply with even greater force to the state in which carbonic acid exists at higher temperatures and under greater pressures than those just mentioned. In the original experiment of Cagniard de la Tour, that distinguished physicist inferred that the liquid had disappeared, and had changed into a gas. A slight modification of the conditions of his experiment would have led him to the opposite conclusion, that what had been before a gas was changed into a liquid. These conditions are, in short, the intermediate states which matter assumes in passing, without sudden change of volume, or abrupt evolution of heat, from the ordinary liquid to the ordinary gaseous state.

"In the foregoing observations I have avoided all reference to the molecular forces brought into play in these experiments. The resistance of liquids and gases to external pressure tending to produce a diminution of volume proves the existence of an internal force of an expansive or resisting character. On the other hand, the sudden diminution of volume, without the application of additional pressure externally, which occurs when a gas is compressed, at any temperature below the critical point, to the volume at which liquefaction begins, can scarcely be explained without assuming that a molecular force of great attractive power comes here into operation, and overcomes the resistance to diminution of volume, which commonly requires the application of external force. When the passage from the gaseous to the liquid state is effected by the continuous process described in the foregoing pages, these molecular forces are so modified as to be unable at any stage of the process to overcome alone the resistance of the fluid to change of volume.

"The properties described in this communication, as exhibited by carbonic acid, are not peculiar to it, but are generally true of all bodies which can be obtained as gases and liquids. Nitrous oxide, hydrochloric acid, ammonia, sulphuric ether, and sulphuret of carbon, all exhibited, at fixed pressures and temperatures, critical points, and rapid changes of volume with flickering movements, when the temperature or pressure was changed in the neighbourhood of those points. The critical points of some of these bodies were above 100°; and in order to make the observations, it was necessary to bend the capillary tube before the commencement of the experiment, and to heat it in a bath of paraffin or oil of vitriol.

"The distinction between a gas and vapour has hitherto been founded on principles which are altogether arbitrary. Ether in the state of gas is called a vapour, while sulphurous acid in the same state is called a gas, yet they are both vapours, the one derived from a liquid boiling at 35°, the other from a liquid boiling at − 10°. The distinction is thus determined by the trivial condition of the boiling-point of the liquid, under the ordinary pressure of the atmosphere, being higher or lower than the ordinary temperature of the atmosphere. Such a distinction may have some advantages for practical reference, but it has no scientific value. The critical point of temperature affords a criterion for distinguishing a vapour from a gas, if it be considered important to maintain the distinction at all. Many of the properties of vapours depend on the gas and liquid being present in contact with one another; and this, we have seen, can only occur at temperatures below the critical point. We may accordingly define a vapour to be a gas at any temperature under its critical point. According to this definition, a vapour may, by pressure alone, be changed into a liquid, and may therefore exist in presence of its own liquid; while a gas cannot be liquefied by pressure, that is, so changed by pressure as to become a visible liquid distinguished by a surface of demarcation from the gas. If this definition be accepted, carbonic acid will be a vapour below 31°, a gas above that temperature; ether, a vapour below 200°, a gas above that temperature.

"We have seen that the gaseous and liquid states are only distant stages of the same condition of matter, and are capable of passing into one another by a process of continuous change. A problem of far greater difficulty yet remains to be solved, the possible continuity of the liquid and solid states of matter. But this must be a subject for future investigation; and for the present I will not venture to go beyond the conclusion I have already drawn from direct experiment, that the gaseous and liquid forms of matter may be transformed into one another by a series of continuous and unbroken changes."

JAMES THOMSON

NOTES

At last a sum of money has been voted for a new Natural History Museum. In introducing the vote the Chancellor of the Exchequer said the British Museum had long been suffering from repletion, and there were no means of exhibiting the valuable articles which, from time to time, were bought for the national collection. Five years ago the trustees resolved in favour of separating the collections, and it had been determined to separate the natural history department from the books and antiquities. For the natural history collection the typical mode of exhibition had been decided on, and the building required must cover at least four acres. Even the present collection would pretty well fill a building of these dimensions, and provision must be made for further extension. The question was, where should this building be situated? and after referring to possible sites he referred to the locality which we were enabled to state some time ago had been chosen—a plot of ground 16½ acres in extent, which the trustees of the Exhibition of 1851 sold to the Government at 7,000*l.* an acre. It therefore cost 120,000*l.*, but is now worth 100,000*l.* more. The sale was coupled with the condition that any building erected upon the land must be for purposes of science and art. For seven years the land had remained waste, a sort of Potter's field, and a scandal to that part of the metropolis. The Government now proposed to place on that piece of land the museum required for the natural history collection. It would occupy four acres; there would be room for wings, and the outside estimate for the building was 350,000*l.*, not an unreasonable price, considering its extent. For the present, however, the Government merely asked for a small vote to enable them to clear the ground, and in order to take the opinion of the House. Railway communication had now made South Kensington easily accessible, and unless a more eligible, a more accessible, and a cheaper site could be suggested, he hoped the Committee would agree to the proposal. He might add that, if it were hereafter thought desirable to do so, there would be room enough on the same site for the Patent Museum, the necessity of which had been much insisted on. We trust that after the discussion which followed the introduction of the vote the scientific men will speak for themselves, and again let their wishes and opinions be heard.

The American Association for the Advancement of Science met yesterday (Wednesday) at Troy. Professor W. Chauvenet is president for the year.

It is gratifying to learn that some of the recommendations of the Royal Commission on Military Education, which were most inimical to the scientific instruction of the army, will not be carried out.

By Imperial decree the *Association Scientifique de France* has been acknowledged to be an *établissement d'utilité publique.*

The French observers are making preparations for a combined attack on the 10th of August meteors.

The list of pensions granted during the year ended the 20th of June, 1870, and charged upon the civil list (presented pursuant to Act 1 Victoria, cap. 2, sec. 6) has been published this week. Among them we note the following:—Mr. Augustus De Morgan, 100*l.*, in consideration of his distinguished merits as a mathematician; Mrs. Charlotte J. Thompson, 40*l.*, in consideration of the labours of her late husband, Mr. Thurston Thompson, as Official Photographer to the Science and Art Department, and of his personal services to the late Princ Consort; Dame Henrietta Grace Baden Powell, 150*l.*, in consideration of the valuable services to science rendered by her husband during the 33 years he held the Savilian Professorship of Geometry and Astronomy at Oxford; Miss Margaret Catherine Ffennell, Miss Elizabeth Mark Ffennell, and Mrs.