Correspondence.

Mr. E. MALLARD stated that the Author's experiments, made by an identical process, were nevertheless much less numerous than those of Messrs. Mallard and Le Chatelier, whose conclusions he had impugned. They were less precise, because the indicator used gave less regular figures than those they had obtained; the Author was also less exact in his discussion of the experiments which related to a subject which required generally great precision. He therefore contended that the Paper did not really contribute to the advancement of the question. The Author criticised, not their experimental results, but their conclusions drawn from those results. His strictures were based principally upon absurdities with which he had gratuitously credited them, but for which they were in nowise responsible. He could not have read attentively either their note in the "Comptes Rendus," which gave the summary and provisional results of their labour, or the complete memoir published in the "Annales des Mines." In substance the Author affirmed that, without taking count either of the loss or heat through the walls, or of dissociations, Messrs. Mallard and Le Chatelier had imagined, in order to put in accord the observation of the temperature with those of the heat of combination, an unjustifiable increase of the specific heat of the gases. Had such been the case, their researches would be unworthy of serious consideration. Had the Author read more carefully, he would have seen that, on the contrary, they had taken extreme care to measure the loss of heat due to the walls. Nearly one-half of their long memoir was devoted to the establishment, from the precise exposition and the careful discussion of each of their diagrams, of the mathematical law of the loss of heat experienced by gaseous mixtures at a high temperature when confined in a closed cold vessel. Mr. Mallard.

The knowledge of this law had in succession enabled them to prove, from the minute discussion of their diagrams, the presence or the absence of dissociation, and if present, to measure its intensity. They had thus been able to prove that, in a certain number of gaseous mixtures, dissociation did not exist, or might be neglected. In these particular cases they had, knowing the loss of heat due to cooling, been able to calculate the maximum pressures which the explosion should have developed if it had occurred

Mr. Mallard. in a vessel impermeable by heat. In the proved absence of dissociation, the maximum pressure thus obtained served them as a basis whence to calculate the true temperature of combustion; which latter served in turn to determine the specific heat of the gaseous products of combustion at the temperature of combustion.

These successive processes seemed to them to be irreproachable. Certainly they might have been deceived in the course of a very delicate and very tedious investigation, applied to nearly one hundred and fifty diagrams, and which had entailed nearly a year's work; but the Author should acknowledge the simple obligation resting upon him of discussing seriously the facts on which their conclusions were based, before characterising such conclusions as erroneous.

He would also remark that the continuous increase of specific heat of carbonic acid was perfectly natural, since this increase was shown in an unmistakable manner between 0° and 200°; it would rather be matter for astonishment if it were suddenly arrested at 200°. As regarded the increase of the specific heats of the perfect gases C, O, N, CO, it appeared to themselves less soundly established than in the case of the specific heats of CO_2 and H_2O; in any case it was much less considerable.

As regarded the novel theory propounded to explain the apparent loss of heat resulting when the observations of the pressures produced by the explosive were combined with those of the heat of combustion, the Author supposed that ignition being propagated rapidly left behind it portions of unburnt gas, which, diluted in a mass already burnt, thereupon combined with it an indefinitely decreasing speed. This phenomenon, besides being purely hypothetical, was only distinguishable from dissociation in that the latter was in equilibrium dependent upon the temperature, while the former would, on the other hand, constitute a state variable with the time. In any case, the effect on the progress of the fall of pressure would be of the same nature as that produced by dissociation. In the mixtures in which they had proved the absence of dissociation, by showing that the law of cooling was the same for high as for low temperatures, they had also proved the non-existence of the phenomenon imagined, without experimental proof, by the Author.

Mr. Rowan. Mr. F. J. ROWAN remarked that the Paper was of great interest from a scientific point of view. It appeared to be certain that the limitation of the observed pressure attained in gas-engines was due to a variety of causes, of which dissociation was an important one. The distinction between inflammation and combustion was

a clear and no doubt a necessary one, but in reasoning from the phenomena observed in the case of solids, even in the fine state of division which was present in coal dust or flour, allowance must be made for the much greater facility of chemical action afforded by the much greater division of the particles of a gaseous body. In the case of a gas it was difficult to conceive that a line could be sharply drawn between inflammation and combustion. The gradual burning of an explosive mixture of gases was not easily accounted for on such an hypothesis. The Author was, of course, familiar with the late Professor Andrews' writings on the gaseous state of matter, and he would therefore ask him if the conclusions arrived at by that investigator did not in his judgment bear directly upon the questions dealt with in the Paper. He referred principally to the general law announced in the following terms: "The dilatation by heat of a body in the ordinary gaseous state, whether measured by its expansion under constant pressure or by the increase of elastic force under constant volume, is not a simple function of the initial volume or initial elastic force, but a complex function changing with the temperature."[1] The variations in the coefficient of expansion under altered conditions of temperature and pressure discovered by Andrews seemed to afford a clue to some of the Author's results, and it was possible they might explain, by analogy, the apparent anomalies in the conclusions of Messrs. Mallard and Le Chatelier referred to by the Author. There might be a critical point for gases at high temperature as there was at low temperatures, the phenomena exhibited by them changing as this point was approached. The element of pressure entered into the question in a most important way, of course. The practical value of the Author's investigations might not be directly apparent to makers of gas-engines, as the important fact to them was that only a certain pressure and temperature could be reached by the explosion of a given mixture of gases, but there was no doubt that practical work must be affected by the accumulation of light on matters of theory.

Mr. Rowan.

Mr. B. H. THWAITE observed that the interpretation of the phenomena relating to the combustion of gaseous explosive mixtures, and connected with a proper development of Carnot's law, was such a vexed question that any trustworthy contribution on the subject should be received with gratitude. Berthelot had made many experiments with apparatus of great precision, and

Mr. Thwaite.

[1] Philosophical Transactions of the Royal Society of London, 1876, vol. clxvi. p. 437.

Mr. Thwaite. the results embodied in his "Essai de Mécanique Chimique,"[1] were a monument to his experimental skill. In this work he described the thermometric, pyrometric and calorimetric apparatus, used for his experiments, by which he confirmed the correctness of Mallard and Le Chatelier's theory as to the variability of the specific heats of liquids and solids with increase of temperature. Along with Vieille, he had extended these investigations to gaseous explosive mixtures, and the results and deductions had been published in the "Annales de Chimie et de Physique." These later experiments afforded supplementary evidence of the correctness of the theory as to the increase of specific "heats" of gases, with increase of temperature, explaining in a measure the cause of the difficulty of obtaining the full thermo-dynamic efficiency due to the explosion of combustible gases in gas-motor cylinders. In Berthelot's experiments, isomeric gaseous mixtures were used of such a character, that after explosion they terminated with a chemically similar constitution. The Author was of opinion, judging from the results of his own experiments, that erroneous conclusions had been drawn from these experiments of Mallard and Le Chatelier, and Berthelot, and Vieille; and the explanation of the phenomena was thus reinstated in obscurity. Unfortunately, the experiments and experimental apparatus used by the Author were not of so complete a character as to permit of rigid and indisputable conclusions to be drawn therefrom. The correct interpretation included the accurate knowledge of so many actions, not yet satisfactorily explained, that it deserved the attention of an international committee of savants in order to solve the questions once for all. Hirn's theory was upheld by Hallauer, and disputed by Zeuner. There was the law of Dalton, and that of Dulong, and Petit. Bunsen's theory of dissociation was upheld by Deville; and combated by Mr. Frederick Siemens and others. The theory of increase of specific heat, advanced by Mallard and Le Chatelier, and upheld by Berthelot and Vieille, was now disputed. There was also Avogadros' hypothesis, and Boyle and Mariotte's law, besides uncertain information relating to diathermancy and the kinetic theory of gases. Until these subjects, especially those relating to specific heat and dissociation, were more clearly understood from reliable data, it was, to say the least, premature to rigidly formulate either a law or an hypothesis. He had designed an experimental apparatus to obtain

[1] Essai de Mécanique Chimique fondée sur la Thermochimie. 2 vols. Paris, 1879.

data of a more trustworthy and complete character, using agents and apparatus of which an accurate knowledge had been acquired. Mr. Thwaite.

Professor Dr. Aimé Witz, of Lille, concurred entirely with the Author's third conclusion, namely, that "combustion is very similar to other chemical actions, the first part of the reaction occurring rapidly, and proceeding with increasing difficulty as the combination approaches completion." His own researches—of which he published the results in the Annales de Chimie,[1] and in the Comptes Rendus of the Paris Academy of Sciences [2]—had even led him to formulate the same law. Thus, he had shown that a mixture of 1 volume of gas with 9·4 volumes of air required 0·21 second to achieve its complete combustion. He had further shown that with excessive dilution, combustion always remained incomplete.[3] But he could not admit that the duration of a combustion depended only on the richness of the explosive mixture, and here he differed from the Author. In fact, if a mixture of gas and air were exploded behind a movable piston, it could readily be shown that the time necessary for effecting combustion varied with the rate of expansion, $\frac{dl}{dt}$. Of this the following was a proof:— Prof. Witz.

Composition of the Mixture.	Rate of Expansion. Metres.	Time of Explosion. Second.
1 volume of gas + 6·33 volumes of air .	4·30	0·045
Ditto	1·70	0·141
1 volume of gas + 9·40 volumes of air .	0·64	0·219
Ditto	0·25	0·468

The Author, by using a single closed cylinder, had not adopted a favourable mode of discovering the true law of explosion; this law could only be observed by using many cylinders of notably different volume, which he had not done. He objected that their results appeared erroneous because the maximum pressure of explosion did not diminish when using chambers of different capacities. How could the pressure diminish, seeing that its maximum value was attained in a period of $\frac{3}{100}$ second? Had he (Dr. Witz) not proved that it was the cooling of the walls which modified the time of explosion? Now cooling was not sensible at the end of $\frac{3}{100}$ second. The Author's objection, therefore, was not well founded.

The great thing that governed explosive phenomena was the

[1] Annales de Chimie et de Physique, vol. xxx. 5th series, 1883.

[2] Comptes rendus de l'Académie des Sciences, vol. xcix. 20 July, 1884; vol. c. 27 April, 1885.

[3] *Ibid.* vol. c. 10 Feb. 1885.

Prof. Witz. cooling of the walls. Dr. Witz had many times shown this to be so; he had above all shown that the useful effect reached a maximum when the rate of expansion, $\frac{dl}{dt}$, reached a maximum, and he had completely explained all the peculiarities observable in gas-engines. The influence of initial compression could only be explained by attributing it to a lesser loss of heat through the walls.

Manufacturers had applied the principles he had made known, and he proved on the 7th of November, 1885, that a gas-engine, made by the firm of Powell, of Rouen, only consumed 562 litres of gas per HP. per hour. This result was due to a strong initial compression, to a high rate of expansion, and to a high temperature of the walls of the cylinder. Practice had, therefore, confirmed his opinions, and for this reason he was constrained to think that the Author was wrong in disregarding the effect of cooling by the walls.

Mr. Clerk. Mr. CLERK, in reply to the correspondence, said he had endeavoured to state fairly Mr. Mallard's views, and was unable to discover in the Paper any substantial misstatement; he had followed Messrs. Mallard and Le Chatelier's investigations with great interest, and he did not call in question the accuracy of the experiments, which indeed his own corroborated. He quite understood that an endeavour had been made to deduce from them the mathematical law of the loss of heat by gases at high temperatures, and that Mr. Mallard's theory of increased specific heat rested on a supposed knowledge of this law; but this was the very point where he differed from Messrs. Mallard and Le Chatelier. He considered that the law of the loss of heat from a highly-heated gas to its enclosing cold walls could not be determined by observations on gaseous explosions when combustion was admittedly proceeding. In his opinion it was impossible to discover this law experimentally, unless it was perfectly ascertained to begin with that no heat was added to the gas experimented on during cooling; that was, that all the heat supplied to the gas was supplied at the moment of attaining the maximum temperature. The law of cooling deduced from the study of the falling line from a gaseous explosion could not be considered as the law of cooling of a highly-heated gas from the same maximum temperature. He agreed that Mr. Mallard's successive processes were irreproachable, but in his opinion the first step was inadmissible; it assumed the very point which should have been proved, and which could not be proved from any experiments made with gaseous explosions.

Mr. Clerk.

In suggesting a possible explanation of the deficit, in supposing a change in Charles's law, such as occurred at the "critical point" in carbonic acid gas, Mr. Rowan would of course have remembered that Professor Andrews' investigation was conducted at a point where the liquefaction of the gas was imminent. It was very improbable that Charles's law should fail at high temperatures; if it did, then the very means of measuring high temperatures failed; all high temperatures were measured by means of the air-thermometer, and if that was incorrect it was difficult to see how high temperatures could be measured at all. He was glad that Mr. Rowan coincided with him in the necessity of a distinction between inflammation and combustion. Mr. B. H. Thwaite was surely in error in supposing such a complete knowledge of all the complex phenomena of gases as was required to apply Carnot's law in practice. It was only necessary to know the fact of the deficit of pressure upon explosion, without understanding its complex causes, to apply practically the reasoning of Carnot's cycle.

The fact of Professor Dr. A. Witz's agreement with his third conclusion gave Mr. Clerk great pleasure. Dr. Witz's independent experiments formed a gratifying corroboration. He was much interested in Dr. Witz's able work, "Études sur les Moteurs à Gaz Tonnant," where his experiments on explosion in a cylinder fitted with a moving piston were described. He had obtained similar results from an Otto and Langen atmospheric engine, which corroborated Dr. Witz's experiments. It was doubtless true that the cold walls regulated explosive phenomena to a very great extent, and were at present great causes of loss in gas-engines. High compression and great expansion, together with enclosing walls at a high temperature, were matters he had at all times attempted to carry into practical work. On this point he was in complete accord with Dr. Witz.