Correspondence.

Mr. A. C. EGERTON thought that some of the phenomena discussed by the Author were probably connected with the excitation and afterglow of carbon dioxide, and Miss M. Kaczynska had shown that the latter could last for a considerable time. The spectrum of the afterglow of CO_2 had been studied by Prof. A. Fowler: in returning from the excited state to the normal state the CO_2 emitted a characteristic banded spectrum.[1] The same spectrum had been observed in the afterglow in the products of combustion after passage of the flame front by Messrs. Withrow and Rassweiler in their experiments with the internal-combustion engine. Their experiments led to the conclusion that combustion was complete in the combustion front, but that excited OH and CO_2 existed in the products which gave rise to the afterglow. There was a certain energy-change, due to the return of the molecule to the normal state, which could be estimated if the number of excited molecules were known, but it was not thought that that would be a considerable portion of the total energy. Mr. Egerton.

Dr. F. W. LANCHESTER remarked that the Paper appeared for the first time to concentrate attention on the difference between live flame and merely hot gas; he found himself in hearty accord with the Author in making that distinction. The old controversy between dissociation and increase of specific heat, as accounting for the suppression of heat in the working fluid in an internal-combustion engine, had always seemed to him to be futile. He thought it was perfectly clear that actual complete dissociation would only take place when an equilibrium point was reached at which the generation of heat by combustion would be zero. That was not a definite temperature as taken by a pyrometer, because of the variation in the velocity of the molecules constituting the total mass of combustion gases—each molecule might be said to have its own temperature—but the principle was not affected. It appeared that as the temperature rose the heat of combustion diminished and the zero value was approached, at which point complete dissociation took place, and such diminution might be interpreted with equal propriety as incipient dissociation (or loosening of the bonds) or as a change of specific heat; it was more a matter of definition than anything else. That was perhaps an unusual view of the old controversy, but one that was clearly legitimate. Dr. Lanchester

[1] Proc. Roy. Soc. "A," vol. 142 (1933), p. 362.

Dr. Lanchester. The Author's point of view, as disclosed in his Paper, however, constituted a departure from that field of ancient controversy, and accorded with an opinion that Dr. Lanchester had held for many years, namely, that a flame was a living thing with a life history, and that without taking that fact into account it was not possible to elucidate all the happenings in an explosion-vessel or in the working cylinder of an internal-combustion engine.

It was known that the value of γ in any gas was related to the number of degrees of freedom by the equation

$$\gamma = 1 + \frac{2}{n}$$

in which n denoted the number of degrees of freedom. Thus, for the monatomic gases such as helium, in which $n = 3$, $\gamma = 1{\cdot}666$, and for the majority of other gases, in which $n = 5$, $\gamma = 1{\cdot}400$. Now, during the period of combustion when molucules were breaking up, exchanging partners, and being reconstituted, it would seem more than probable that there were more degrees of freedom than in either the initial or final states, and so a temporarily lower value of γ, which was found to be the case. It seemed that flame radiation as distinct from hot-gas radiation lent support to that doctrine, because such distinctive radiation betokened some form of atomic freedom otherwise not present. Nearly 40 years ago Dr. Lanchester had proposed a form of calorimeter from which he had great hopes; by the kindness of the late Prof. Poynting he was granted facilities in the Laboratory of the Department of Physics in the (then) Mason College, and several attempts were made to bring the scheme to fruition, but with very meagre success. The principle involved was that if any definite quantity of heat were injected by any means into an enclosure containing a perfect gas, the pressure rise would be independent of the distribution of that heat. The apparatus consisted of a cylindrical vessel of 18 litres capacity, approximately 6 inches in diameter by 3 feet in length, set up vertically; a few cubic centimetres of combustible gas were admitted through a simple jet burner, and the resulting pressure was measured by a delicate dead-beat manometer of special design. Such a calorimeter would obviously have been a very useful instrument, since calorific values of coal-gas or fuel-gas could have been determined from small samples, easily conveyed (bottled) from one place to another, and the whole time required for a determination would have been only 2 or 3 minutes at most. Also, the fact that the energy emitted by radiation would not be recorded meant that the value given would represent more closely the utility of the fuel for the purpose of driving a gas-engine, than if, as in the Junker instrument, the total heat were included. After the usual crop of petty difficulties and alterations, all necessary adjustments were made and the manometer calibrated; tests were then carried out using hydrogen as the fuel. In spite of the most careful precautions it was not found possible to record more than $\frac{3}{4}$ of the total heat of the fuel. Thus, using 5·76 cubic centimetres of hydrogen at 14° C. and 763 millimetres barometer, the gram-calories per gram worked out at 21,988 and 23,223 (according to typical records which had been preserved), as against the true value when hydrogen was burned to form water vapour, namely, about 29,000. A discrepancy was thus found of the same order of magnitude as that recorded in the pressure chambers of Clerk and others, and not very far from estimates based on the conditions which obtained in the working cylinder of an internal-combustion engine, and yet the conditions were very different. Owing to pressure of work and the absence of any money grant or other assistance the scheme was abandoned. The cause of the discrepancy remained an enigma. It did not seem explicable on the ground of loss by radiation, as such loss should not be as high as 25 per cent. of the total heat. His estimate at that date (1892–3) was that loss by direct radiation in a gas-engine cylinder should lie between 5 per cent. and 10 per cent. Cooling from the walls of the chamber could not account for any material loss, since the flame only existed for a few seconds at the most, and the size, and particularly the height, of the vessel precluded any possibility of loss of that character. There was a bare possibility that some hydrogen passed into the surrounding air unburnt. **Dr. Lanchester.**

Mr. M. S. KUHRING [1] remarked that on pp. 172 and 173 the Author stated his belief that only 70 per cent. of the fuel energy was converted into thermal or pressure energy in gas engines at the moment indicated by the peak pressure of the indicator diagram, and gave two probable reasons why the degree of incomplete combustion was greater in the internal-combustion engine than in the gaseous explosion vessel (at peak pressure); firstly, that in engines the explosion was speeded up by turbulence, so that at the moment of peak pressure no part of the charge had had time to reach as complete combustion as in the stagnant charge, and secondly, that there was a larger ratio of surface to volume in the combustion chamber of an engine than in a sphere, so that any delay that occurred in the boundary layer had a greater influence in the engine than in the spherical explosion vessel. It was true that the surface area was greater in the engine, **Mr. Kuhring**

[1] The following contributors to this correspondence are on the staff of the National Research Council of Canada:—Messrs. M. S. Kuhring, J. H. Parkin, D. C. Rose, and R. Ruedy.—SEC. INST. C.E.

Mr. Kuhring. but in that case there was considerably more turbulence, even under the worst conditions, which tended to thin down the boundary layer, and that would in turn tend to reduce the amount of the charge which was not completely burnt at peak pressure. If some means could be introduced to break up the boundary layer, the combustion might be more complete, but there was also the question of heat insulation, and such breaking-up of the boundary layer might permit enough heat-loss to the walls to more than offset the gain attained by more complete combustion. There might also be some bad effects on the oil film on the cylinder wall.

In connection with the photograph in *Fig. 3* where the gas was luminous, cooled, and was again luminous, that was not necessarily due to any abnormal condition of CO_2 or H_2O, but might be due rather to the stripping-off of the boundary layer, which, owing to the cooling action of the cylinder walls, resisted combustion on the expansion or working stroke, and on the second compression stroke was replaced in part by the exhaust gas, owing to turbulence. That was repeated on succeeding compressions until it was all oxidized, and no further luminosity appeared.

On pp. 174–175 the Author remarked "(1) that apparently no uncombined gas is present during the adiabatic compression subsequent to the explosion-expansion stroke, for all tests agree in showing that combination is complete in the exhaust gases in normal running and the temperatures are too low for dissociation to occur; consequently the luminosity subsequent to the explosion-expansion stroke cannot be explained in terms of chemical activity; and (2) that normal gases like CO_2, H_2O, O_2 and N_2 remain dark if heated by thermal means to temperatures at which the exploded gases in the engine-cylinder are luminous." In the first place, conditions in a normal engine were not necessarily the same as those when the engine was run through a series of cycles and only one charge was introduced. In other words, the expanded charge was compressed and re-compressed several times, instead of being forced out of the cylinder. If the boundary layer was responsible for the luminosity observed, then section 2 did not apply. Very few engines operated normally without some products of partial combustion being found in the exhaust.

The passage on p. 176, indicating the possibility that there might be some latent energy in the gases at the end of the expansion stroke, brought out a strong argument for double-expansion engines and also other exhaust-gas utilization equipment, which had been attempted from time to time, but would not the additional energy be due to the boundary layer, which might be partially detached during the exhaust stroke? It was rather surprising that the heat-energy found in the exhaust for a weak mixture exceeded that found for a strong mixture. It would be expected that that would be reversed, in view of the air/fuel ratio, and also in view of the higher temperatures which occurred with weak mixtures. Mr. Kuhring.

It would be of interest to consider the effect of knock-inhibitors in connection with the work described in the Paper. As the compression ratio or compression pressure was raised, it became necessary to add an anti-knock substance, generally lead tetraethyl, which tended to slow-down combustion. A knowledge of its effect on the percentage of net fuel energy found in the exhaust gases might be of considerable value. It might also be expected that there would be a considerable difference in the results obtained in high- and low-speed engines, owing to the time factor.

Mr. J. H. Parkin remarked that he was not convinced of the validity of the inference in the Paper that combustion in an internal-combustion engine resulted in the formation of molecules of water and carbon dioxide in an abnormal condition, by virtue of which they had associated with them energy in some latent form, which latent energy might be used to increase the available power from the engine. It seemed to him that the conditions under which such tests had to be made, the number of variables entering into the question, and the deficiencies in the measuring instruments must be such as to have a serious masking effect, as a result of which deductions from the observed differences were difficult to make with certainty. The boundary layer and turbulence were two factors whose effect might have been under-estimated in the Paper. Mr. Parkin.

Dr. D. C. Rose observed that it was well known that the exhaust gases of internal-combustion engines were charged, the gases being in an ionized state. Urgand[1] had made measurements on the charge acquired by engines due to ionized exhaust gases. Dr. Rose had made the following very rough calculation to see if excitation or ionization of the gases could account for enough energy to have a noticeable effect on a gas-engine. Considering an engine having a displacement of approximately 500 cubic centimetres, it was assumed that the exhaust gases when reduced to N.T.P. occupied a volume in the gaseous state of 500 cubic centimetres, or that there were an equivalent number of molecules to such a volume of gas in the exhaust gases from each explosion stroke. Now each molecule, if in an excited or ionized state, might carry away with it energies up to the ionization voltages of the gas concerned. As a basis of calculation, it was supposed that 0·01 per cent. of the molecules were excited to a potential of 5 electron volts. The energy carried away was then calculated as follows :— Dr. Rose.

[1] *Annalen der Physik*, vol. 85, pp. 331–361. 1928.

Dr. Rose.

500 cubic centimetres of gas at N.T.P. contained $500 \times 2{\cdot}7 \times 10^{19}$ molecules.

Each excited molecule carried away $\frac{5 \times 4{\cdot}77 \times 10^{-10}}{300}$ ergs of energy.

Therefore the energy lost by such excitation if 0·01 per cent of the molecules were excited was—

$$\frac{500 \times 2{\cdot}7 \times 10^{19} \times 5 \times 4{\cdot}77 \times 10^{-10}}{300 \times 10^{4}} \text{ ergs}$$
$$= 1{\cdot}073 \times 10^{7} \text{ ergs}$$
$$= 1{\cdot}07 \text{ joules or } 0{\cdot}25 \text{ calorie.}$$

He was not sufficiently familiar with engines to make an "off hand" comparison between that figure and the heat of combustion of one power stroke, but, assuming that such an engine as mentioned above running at 1,800 revolutions per minute developed 15 H.P. per cylinder, a comparison could be made;

15 HP. $= 15 \times 746$ watts $= 11{,}190$ joules per second, and 1,800 revolutions per minute $=$ 15 power strokes per second, hence the energy per power stroke $=$ 746 joules or 178·4 calories.

Comparing that with 0·25 calorie lost due to excitation, it was evident that that loss was negligible. Now 0·01 per cent. of the atoms being in an ionized or excited state represented a very high density of ionization or excitation in a normal gas. He did not know whether it was an unreasonably high or an unreasonably low figure for gases in an engine. If it were from ten to a hundred times higher it would account for the discrepancies found by the Author. Nitrogen was particularly well known to have metastable states in which it might remain for some time. The question might be investigated by a spectroscopic examination of the gases as they passed the exhaust valve. He agreed with Mr. Parkin that with the number of variables and the types of instruments used in engine work it was very difficult to sift out a possible effect due to energy stored in the gases of combustion.

Dr. Ruedy.

Dr. R. RUEDY observed that the experiments described were not sufficiently accurate to prove that 3 per cent. or more of the charge in an internal-combustion engine escaped as a rule with the exhaust gases before it had become ignited. Firstly, the pressure-differences observed in the first part of the Paper were such as might be expected from the difference in specific heat; hydrogen had the lowest specific heat and would thus give the highest temperatures and pressures; it was followed by nitrogen and then by oxygen (Table I). Secondly, in the second series of experiments the instantaneous heat-loss should have been taken into account in place of an average correction. Lastly, so long as the spectrum emitted by the "flame" produced during the second compression had not been examined, it was not possible to state whether the light was due to afterburning or to emission from solid metal or carbon particles or surfaces, or to both. Moreover, the amount of charge giving out the light might be much smaller than 1 per cent. Dr. Ruedy.

The AUTHOR, in reply, remarked that it was unfortunate that his Paper had been written before the publication of the paper on the after-glow of CO_2 by Professor Fowler and Mr. Gaydon, for it would have helped him greatly in the presentation of his views—particularly those described in the Appendix. He was grateful to Mr. Egerton for his reference to it. Professor Fowler and Mr. Gaydon gave alternative explanations of their work which were very similar to the alternative explanations which he had given in the Appendix (p. 181) as follows:— The Author.

"A reasonable hypothesis would appear to the Author to be that combination in the gaseous phase of fuel and air mixtures results in the formation of CO_2 and H_2O molecules of abnormal structure, in virture of which they *either* contain more intra-molecular energy than normal CO_2 and H_2O at corresponding temperatures, *or* ionize or dissociate at these temperatures in some manner quantitatively widely different from that of the ordinary thermal dissociation of normal gases." On the whole Professor Fowler seemed to favour the view that the spectrum of the after-glow was due to CO_2 returning from its excited state to the normal state. But as Mr. Egerton pointed out, the great difficulty, in applying that as a complete explanation of the Author's experiments was quantitative. In the constant (atmospheric) pressure burning of CO there would appear to be nearly as much latent energy per gram-molecule of freshly formed CO_2 as there was internal or thermal energy of normal CO_2 under similar conditions. The Author felt unable to decide as between the two alternative explanations.

He was deeply grateful to Dr. Lanchester for crystallizing his views in such vivid phraseology. The essential difference between the Author's view and that generally held was that the products of combustion constituting flame-gases were widely different in their behaviour from merely hot gases; in fact, that "flame was a living thing with a life history, and that without taking that fact into account it was not possible to elucidate all the happenings in an explosion-vessel or in the working cylinder of an internal-combustion engine." It was with pleasure that the Author found that his view had been anticipated by Dr. Lanchester. He hoped Dr. Lanchester would find leisure to continue with his calorimeter

The Author. investigation, or, at any rate, to publish in some detail his early experiments.

The very useful and stimulating criticism of Messrs. Kuhring and Parkin and Drs. Rose and Ruedy could, it was thought, be best replied to by stating the following facts :—

(i) In dust-free explosions made in glass or quartz vessels the gases first ignited were made brilliantly luminous by the subsequent adiabatic compression caused by the burning of the remainder of the gas. Here the luminosity could not be caused by the oxidation of a stripped boundary layer.

(ii) The spectrum of the after-glow of inflamed gases as observed by Messrs. Withrow and Rassweiler showed clearly that it was in the main associated with OH and CO_2 molecules.

(iii) The latent energy theory was not put forward as a result of engine experiments in which it was agreed that the number of variables made it very difficult to obtain precise information. Such experiments were used in support of theories formed as a result of closed-vessel explosion experiments (Part I) and platinum-thermometry experiments (Appendix).

He would express his thanks for the generous references which had been made in regard to his work and for the carefully-considered contributions to the Discussion and Correspondence. Long experience of combustion-research had convinced him that profound modification of the simple combustion-theory now generally held was necessary if combustion-phenomena generally and internal-combustion engine phenomena in particular were to be adequately explained and further progress made. He would like to say that the latent-energy theory had up to the present stood the test of a considerable volume of experimenting which had been proceeding in his laboratory since the Paper was written, and he offered the theory, as developed in the Appendix, as a step towards a more comprehensive theory.