

Gaseous Combustion at High Pressures.<sup>1</sup>

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## INTRODUCTION.

IN the course of the researches upon gaseous combustion which for many years past have been carried out in my laboratories, it became necessary to study the subject under much higher pressures than those heretofore employed. As this aspect of the work has recently assumed greater importance from the point of view of the mechanism of combustion than was at one time foreseen, an outline of it may be of interest. Before, however, explaining what our new observations have been, something should be said about the apparatus and methods employed for such work. For they must obviously differ from those used for experiments at atmospheric pressure, where the conditions are much less severe.

In the first place, the experiments must be carried out in specially designed bombs of forged steel capable of withstanding the sudden development of very high explosion pressures. Thus, in our recent experiments, the initial pressure at which the combustible mixtures were fired ranged up to 100 atmospheres; and the resulting pressures, which were developed in a small fraction of a second, were anything up to ten times as great. Hence the method of measuring and recording the pressures must be capable of following accurately, and with the least possible lag, a rise of pressure of from (say) 100 to 1000 atmospheres occurring within  $\frac{1}{200}$ th of a second. For this purpose we have employed a recording manometer of the form designed by Sir J. E. Petavel, which is a most efficient appliance for high-pressure explosion work.<sup>2</sup>

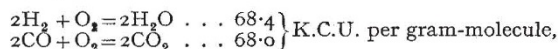
The photographic pressure-time records obtained in our experiments show (1) the rate at which the potential energy of the explosive mixture fired is transferred into kinetic (*i.e.* pressure or temperature) energy of the products; (2) the ratio of the maximum pressure attained on explosion to the initial pressure at which the mixture was fired—usually denoted as  $P_m/P_i$ ; and (3) the rate of the subsequent cooling. From a study of these and other features of the records we are able to draw conclusions as to certain fundamental aspects of the combustion process itself.

## SOME FEATURES OF THE COMBUSTION OF HYDROGEN AND OF CARBON MONOXIDE IN AIR.

As an example of the potentiality of high-pressure explosion research to reveal and elucidate new factors in gaseous combustion, I propose to deal mainly with the cases of hydrogen and carbon monoxide. For although at first they may seem to be of the simplest type, yet they present features of extraordinary interest and complexity which for many years past chemists have vainly tried to explain. Even engineers, who study internal combustion problems in their own way, without troubling themselves overmuch with the mechanism of the chemical changes involved, are

seeking light upon what is termed the "suppression of heat" in such explosions. Indeed our present ignorance about these matters shows how far we are from really understanding the elements of gaseous combustion, and the need there is of much further fundamental research thereon.

From a chemical point of view there has always been something enigmatical about the very different behaviours of the two simplest combustible gases, hydrogen and carbon monoxide, when burning in air. For although their volumetric heats of combustion (assuming the initial and final temperatures being both about 15° C.) and the proportion by volume in which each of them combines with oxygen are the same, namely:



yet in many respects their modes of combustion in air present a striking contrast.

Thus, for example, (1) the appearance of a flame of hydrogen in air is very different from the lambent blue flame of carbon monoxide burning at the same orifice and under the same pressure; (2) hydrogen-air mixtures have lower ignition temperatures, and, under similar physical conditions, propagate flame much faster than the corresponding carbon monoxide-air mixtures; (3) the presence of even a minute quantity of steam greatly assists, if it is not absolutely essential to, the oxidation of carbon monoxide in flames, even when detonation is set up—thus a flame of the dry gas is easily extinguished on being introduced into a jar of air that has been previously dried over strong sulphuric acid; (4) a flame of carbon monoxide burning in air loses by radiation nearly 2.4 times as much energy as a hydrogen flame of the same size; also (5) the two radiations have their own characteristic wave-lengths—namely, 2.8  $\mu$  from a carbon monoxide-air flame and 4.4  $\mu$  from a hydrogen-air flame—which have been attributed to vibrational conditions in incipiently formed CO<sub>2</sub> and HO<sub>2</sub> molecules respectively, or, as I prefer to say, to the formation *at the moment of combustion* of intensely vibrating carbon monoxide-oxygen and hydrogen-oxygen complexes, which ultimately give rise to carbon dioxide and steam molecules respectively.

To summarise: carbon monoxide burns in air more slowly and with a more highly radiating flame than does hydrogen; also apparently the presence of some steam or other hydrogen-containing substance is necessary for its combustion. Precisely how steam accelerates or determines the combustion of carbon monoxide (and only a minute quantity suffices) has up to now never been completely explained; but chemists are generally agreed that carbon monoxide molecules are particularly inert towards oxygen molecules in flames. Indeed I think there are grounds for believing that in ordinary flames carbon monoxide cannot react with undissociated oxygen molecules, but that it requires the presence of either :O atoms or "activated steam" :OH<sub>2</sub> molecules.

<sup>1</sup> From a discourse delivered at the Royal Institution on Friday, May 11.  
<sup>2</sup> A full description of the bomb and accessory appliances will be found in Phil. Trans. Roy. Soc., A 215 (1915), pp. 275-318.

## HIGH-PRESSURE EXPERIMENTS.

Bearing the foregoing considerations in mind, let us now see what new light has been shed on the problem as the result of high-pressure combustion research. Here it should be pointed out that, inasmuch as the chief difference between the condition of high- and low-pressure experiments lies in the absolute concentration of the interacting molecules, it may be expected that factors the operation of which chiefly depends on such concentration will become more dominant as the pressure arises. Indeed, the value of high-pressure work lies in the fact that it tends to show up and accentuate the operation of factors the influence of which may be either masked or overlooked at ordinary pressures.

One of the first things disclosed by our experiments was the absence of any direct relation between the rate at which the potential energy of an explosive mixture is transferred on explosion to its products as sensible heat (pressure) and the magnitude of the chemical affinity between its combining constituents. Thus, for example, the time required for the attainment of maximum pressure on exploding at 50 atmospheres a methane-air mixture ( $\text{CH}_4 + \text{O}_2 + 4\text{N}_2$ ), in which the combustible gas and oxygen are present in equimolecular proportions (*i.e.* corresponding to the primary chemical interaction in the flame), was many times longer than that required in the case of the corresponding hydrogen-air mixture ( $2\text{H}_2 + \text{O}_2 + 4\text{N}_2$ ), notwithstanding the fact that the affinity of methane is at least twenty, and possibly as many as thirty, times as great as that of hydrogen for oxygen in flames. In other words, the avidity with which a combustible gas seizes upon oxygen in flame combustion is not necessarily the factor which mainly determines the rate at which the potential energy of the mixture is transferred into kinetic energy of its products.

Later experiments have chiefly dealt with the explosion usually at an initial pressure of 50 atmospheres of what may be termed isothermic mixtures of either carbon monoxide or hydrogen with sufficient oxygen for complete combustion *plus* some variable diluent developing as nearly as may be the same amount of energy on combustion. I will now endeavour to explain their significance.

## THE CONTRAST BETWEEN CARBON MONOXIDE-AIR AND HYDROGEN-AIR PRESSURE CURVES.

We may appropriately begin with a consideration of two typical pressure-time records (Fig. 1) obtained when normal carbon monoxide-air and hydrogen-air mixtures ( $2\text{CO} + \text{O}_2 + 4\text{N}_2$  and  $2\text{H}_2 + \text{O}_2 + 4\text{N}_2$ ) were respectively fired in the bomb at an initial pressure of 50 atmospheres.

Now, although these two mixtures developed as nearly as may be the same total amount of energy on explosion, there was a striking contrast between the character of the pressure-time curves obtained. For whereas in the typical hydrogen-air curve the pressure

rose with extreme rapidity (actually in 0.005 second) to its maximum (about 400 atmospheres), and almost immediately thereafter began to fall and assume the character of a simple cooling curve, in the corresponding carbon monoxide curve the pressure rose much more slowly and only attained a maximum (about 410 atmospheres) after 0.18 second, after which it was maintained almost at its maximum for a considerable time interval. The comparative slowness with which pressure energy is developed in such a carbon monoxide-air explosion, together with a considerable exothermic effect after the maximum pressure had been reached, were indeed very remarkable and significant features of our experiments. At first we were inclined to attribute them to the supposed "slow-burning" property of carbon monoxide as compared with the "quick-burning" of hydrogen; but further experiments revealed the operation of another totally unexpected factor—namely, the presence of nitrogen, which, as we discovered later, is not inert but acts as an "energy-absorber" in the combustion of carbon monoxide at such pressures.

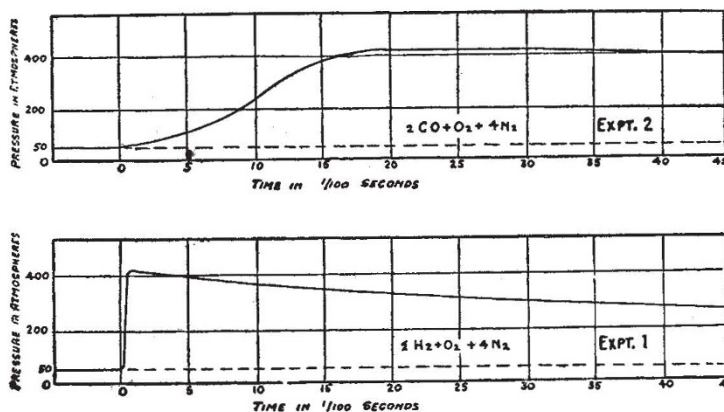


FIG. 1.—Pressure-time records for the explosion of carbon monoxide-air and hydrogen-air mixtures.

## EFFECT OF ADDITION OF HYDROGEN UPON THE CARBON MONOXIDE-AIR CURVE AND UPON A CARBON MONOXIDE FLAME BURNING IN AIR.

It was next discovered that the replacement, even in very small proportions, of carbon monoxide by its equivalent of hydrogen in the aforesaid normal carbon monoxide-air mixture had a disproportionately large influence in accelerating the rise of pressure on explosion. This remarkable result, which is of considerable theoretical import, was dealt with at length in a paper published two years ago by the late W. A. Haward and myself in the Proceedings of the Royal Society.<sup>3</sup> Indeed at first sight it seemed as if the hydrogen had imposed its own character upon the whole course of the carbon monoxide combustion, even when the combustible part of the mixture exploded contained only one part of hydrogen to twenty-three parts of carbon monoxide by volume.

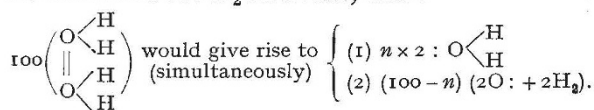
In this connexion it may be mentioned that the addition of a moderate amount of hydrogen to carbon monoxide burning in air at ordinary pressure has a considerable effect upon the character and spectrum of

<sup>3</sup> Proc. Roy. Soc., A, 100 (1921), pp. 67-84; see also a further paper in the current (August) number of the Journal of the Chemical Society.

the flame, a circumstance which seems to be of some significance in relation to the mechanism of carbon monoxide combustion. In conjunction with Prof. A. Fowler, of the Imperial College, South Kensington, we are now investigating it more closely with the view of finding out its meaning. But the facts known warrant us in concluding that the addition of a comparatively small proportion of hydrogen has a peculiar influence upon the combustion of carbon monoxide, whether at high pressures (as in our bomb experiment) or in flame combustion at ordinary pressures.

#### THE MECHANISM OF THE COMBUSTION OF CARBON MONOXIDE.

To explain the peculiar influence of hydrogen or steam upon the combustion of carbon monoxide, I think it must be supposed that oxygen and carbon monoxide molecules are mutually inert in flames, and that before the carbon monoxide can be oxidised the  $O_2$  molecules must be resolved either into O atoms or into "activated" steam. This precedent condition can be brought about by the presence of hydrogen (or maybe steam) in the mixture undergoing combustion. For, according to my present view, an undissociated  $O_2$  molecule on being heated in the flame has its "residual affinities" sufficiently stimulated to enable it to seize upon two hydrogen molecules, forming initially an unstable vibratory complex  $H_4O_2$ . Such a complex, being in an intensely vibratory condition, would instantly break down (1) *parily* into two molecules of steam, also in a vibratory (and therefore "activated") condition, and (2) partly also into two :O atoms and two  $H_2$  molecules, thus :



The ratio  $n/(100 - n)$  would obviously depend upon both temperature and environment. The higher the temperature and the less hydrogen in the environment the less the magnitude of  $n$ . But in all conditions the hydrogen in a combustible mixture containing also carbon monoxide functions as a resolver of  $O_2$  molecules simultaneously into (1) "activated" steam and (2) :O atoms. Thus it is suggested that the primary function of hydrogen as a promoter of the combustion of carbon monoxide is to resolve the  $O_2$  molecules (inert towards carbon monoxide) into :O atoms and "activated"  $OH_2$  (reactive towards carbon monoxide), itself being continuously regenerated in the process, as is shown in Fig. 2.

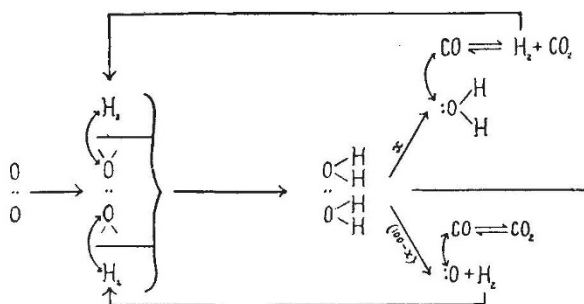
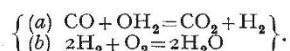


FIG. 2.

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It may be observed that this view is similar to the one advanced forty years ago by Prof. H. B. Dixon to explain his discovery of the mutual inertness of dry carbon monoxide and oxygen in flames, but modified in one particular so as to make it more applicable to the further facts now known. He supposed that carbon monoxide is oxidised by  $OH_2$  (but not by  $O_2$ ) molecules in flames, the resulting hydrogen being immediately burnt to steam, which was thus continuously regenerated, as follows :



If, however, only such interactions (and no others) occur, it is difficult to understand why the colour and spectrum of a flame of pure (moist) carbon monoxide are so unlike those of hydrogen burning in air. The characteristic spectrum of a carbon monoxide flame, which extends far into the ultra-violet, would surely seem to be due to the formation in it of some  $CO_2$  molecules in a more highly vibratory state than would be likely to arise merely by interactions of CO and  $OH_2$  molecules. The difficulty in question is obviated, and also other facts would be better explained, by supposing (as I do) that an unstable vibratory  $H_4O_2$  complex, primarily formed by the interaction of  $O_2$  and  $H_2$  molecules, decomposes in each of two ways yielding : $OH_2$  and :O atoms, both of which are capable of oxidising carbon monoxide.

#### THE ENERGY-ABSORBING FUNCTION AND ACTIVATION OF NITROGEN IN THE COMBUSTION OF CARBON MONOXIDE.

It next occurred to us to try the effects of progressively replacing the nitrogen of a normal carbon monoxide ( $2CO + O_2 + 4N_2$ ) mixture by molecular equivalents of other gases, e.g. oxygen, carbon monoxide, or argon. The first two of these gases are diatomic, and would have much the same densities and heat capacities as the nitrogen which they replaced ; and although they might be expected to exert some "chemical mass" influence upon the combustion, yet in all other respects they would act as "diluent." In argon we had an absolutely inert monatomic gas of higher density, but smaller volumetric heat capacity, than nitrogen, and incapable of any internal vibrational energy. It would therefore presumably be incapable of exerting any effect upon the explosion other than that of merely sharing, by molecular collisions, in the increased kinetic energy acquired by the system as the result of the combustion.

It may be observed that while the said replacement of the nitrogen by the other gases would not affect in any way the total energy liberated on explosion, yet the experiments showed that it affected somewhat the proportion of the energy recorded by the gauge as pressure (temperature) at the instant of maximum pressure, and still more so the rapidity with which the said pressure energy was developed. The most important experimental results from this point of view are summarised in the following table, and illustrated by the set of pressure-time curves reproduced in Fig. 3. Here it may be pointed out that the most essential

data which must be established in such experiments are the following :

$P_i$  = the initial pressure in atmospheres at which each mixture is fired.

$P_m$  = the maximum pressure in atmospheres recorded in the explosion.

$t_m$  = the time in seconds required for the attainment of the maximum pressure after ignition.

$\Sigma$  = the thermal equivalent in K.C.U. of the energy liberated during the explosion.

Also the percentage amount by which  $P_m$  falls during (say) 0.5 sec. after  $t_m$ .

Mixture exploded.	$\Sigma$ .	$P_i$ .	$t_m$ .	$P_m$ .	$P_m/P_i$ .	Per cent. Fall in Pressure in 0.5 sec. after $t_m$ .
2CO+O <sub>2</sub> +4N <sub>2</sub>	10.2	50	0.190	409	8.18	11.6
2CO+O <sub>2</sub> +4O <sub>2</sub>	10.0	50	0.005	460	9.20	33.33
2CO+O <sub>2</sub> +4CO	10.4	50	0.019	450	9.00	34.3
2CO+O <sub>2</sub> +4Ar	10.2	50	0.025	510	10.20	26.4

These and other similar results led very decidedly to the conclusion that the nitrogen present in the normal carbon monoxide-air mixture had been exerting a specific influence on the whole course of events, which was manifested in a three-fold effect upon the pressure curves—namely, (1) a marked retardation of the rate of attainment of maximum pressure, (2) a lowering of the maximum pressure, and (3) a considerable retardation of the subsequent cooling. For whenever such nitrogen was wholly replaced by its molecular equivalent of any one of the other three gases, the development of pressure became nearly as rapid as in the explosion of a normal hydrogen-air mixture under like conditions. Moreover, comparative analyses of the pressure-time records obtained during the experiments in question have shown that, when nitrogen was present, much less kinetic (pressure) energy was absorbed up to the attainment of maximum pressure than was subsequently liberated during the cooling period. This remarkable circumstance shows that a considerable part of the radiation emitted by the burning carbon monoxide (which otherwise would have been absorbed by the walls of the explosion vessel) was intercepted by the nitrogen present. Part of the nitrogen so irradiated would then, in favourable circumstances, be oxidised to nitric oxide, thereby absorbing part of the kinetic energy developed by the explosion and consequently reducing the maximum pressure attained. Finally, the radiant energy so absorbed by the nitrogen, *plus* part of the kinetic energy (if any) absorbed in forming nitric oxide during the combustion, was liberated as kinetic energy during the cooling period, so delaying the cooling. Thus it was manifest that under our experimental conditions nitrogen has the power of absorbing part of the radiant

energy developed by the combustion of carbon monoxide, and of slowly giving it out again in a kinetic form during the subsequent cooling period. In other words, nitrogen is not inert, but acts as an "energy absorbing" spring in such explosions. Indeed the results set forth in the foregoing table can scarcely be explained on any other supposition.

Another important conclusion arising out of these experiments is that when nitrogen so absorbs radiant energy developed during a carbon monoxide-air (2CO+O<sub>2</sub>+4N<sub>2</sub>) explosion under such conditions, it becomes chemically "activated," and capable of combining much more readily with oxygen than does nitrogen which has merely been raised to a correspondingly high temperature in a similar hydrogen-air (2H<sub>2</sub>+O<sub>2</sub>+4N<sub>2</sub>) explosion. Indeed, when the bomb was rinsed out with distilled water after one of our hydrogen-air explosions at an initial pressure of 50 atmospheres, no more than a faint trace of nitric acid could be detected on applying the diphenylamine test to the washings; whereas, in the case of the corresponding carbon monoxide-air explosions, a similar

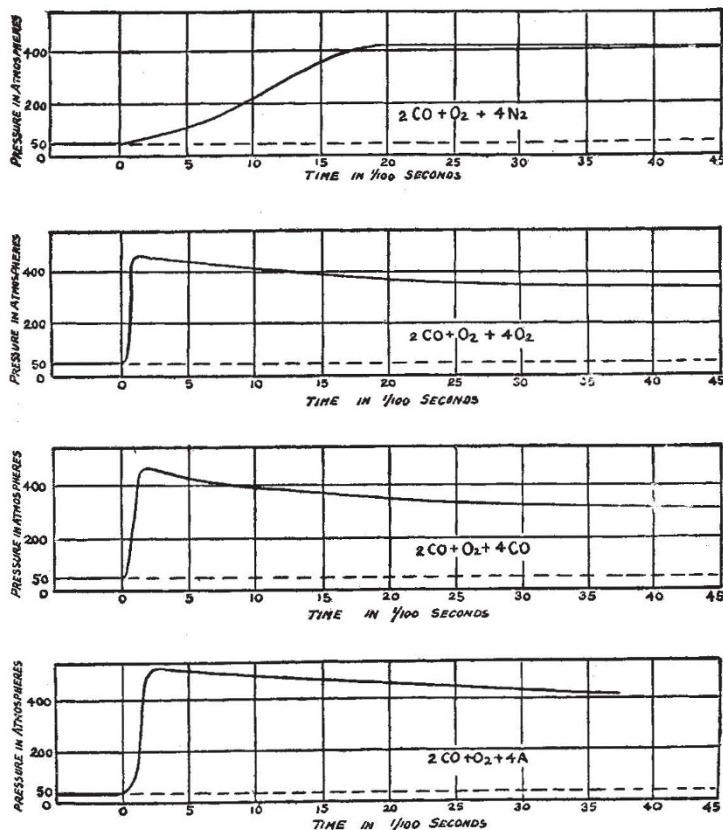


FIG. 3.—Pressure-time records for the combustion of carbon monoxide using different diluents.

test always showed a considerable formation of nitric acid.

It would seem as though the nitrogen molecule is able to absorb the particular quality of radiation emitted as the result of the interactions of CO and :O during a carbon monoxide-air explosion, which is different from that emitted during a hydrogen-air explosion. In other words, it seems as though there is

some constitutional correspondence between CO and  $N_2$  molecules (the densities of which are identical) whereby the vibrational energy (radiation) emitted when the one burns is of such a quality as can be readily absorbed by the other, the two thus acting in resonance. The radiant energy so absorbed during the explosion presumably would not affect the maximum pressure attained, except in so far as the conditions permitted of any secondary oxidation of the "activated" nitrogen to nitric oxide during the actual combustion period; but radiant energy so absorbed would be liberated in a kinetic form during the subsequent cooling period, as the "activated" nitrogen slowly reverted to the ordinary form. Analyses of the pressure-time records obtained have entirely confirmed this supposition.

The following graphs (Fig. 4) illustrate the strength of the evidence obtained up to this point as to the activation of the nitrogen during a carbon monoxide-air explosion at high pressures. They show the rates of cooling (expressed as pressure fall in atmospheres per second) of the gaseous systems immediately after the attainment of maximum pressure, when each of the four mixtures,  $2CO + O_2 + 4N_2$ ,  $2CO + O_2 + 4O_2$ ,  $2CO + O_2 + 4Ar$ , and  $2H_2 + O_2 + 4N_2$ , were exploded in the bomb at an initial pressure of 50 atmospheres.

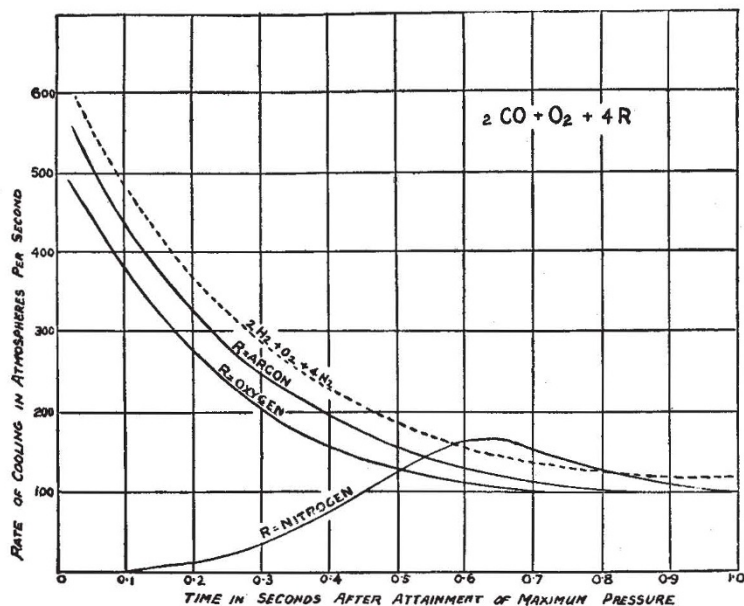


FIG. 4.—Rate of cooling after combustion of carbon monoxide using various diluents.

It will be seen that, except in the case of the carbon monoxide-air mixture, the cooling was perfectly regular, and presented no abnormal features whatever. In the case of the  $2CO + O_2 + 4N_2$  mixture, however, there was no cooling at all during the 0.1 sec. after the attainment of the maximum pressure; and it was not until the lapse of the 0.6 sec. thereafter that anything like a normal rate of cooling was established. Attention is specially directed to the striking contrast between the perfect normality of the first 0.6 sec. of the cooling period in the case of the hydrogen-air ( $2H_2 + O_2 + 4N_2$ ) mixture, and its complete abnormality in the case of

the corresponding carbon monoxide-air mixture. This circumstance, combined with the perfect normality of the cooling in the case of the  $2CO + O_2 + 4Ar$  mixture, can scarcely be explained except on the assumption that the nitrogen functions differently in a hydrogen-air explosion, where it acts as an inert diluent only, from what it does in a carbon monoxide-air explosion, where in addition to its ordinary diluent action it

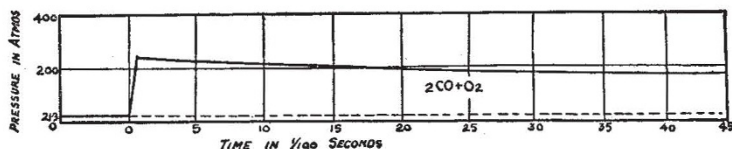


FIG. 5.—Pressure-time record of carbon monoxide-oxygen explosion.

has a peculiar energy-"absorbing" effect, whereby it becomes chemically "activated." On such an assumption the meaning of the  $2CO + O_2 + 4N_2$  cooling curve is that the radiant energy which had been absorbed by the  $N_2$  molecule during the previous combustion period was being slowly evolved in a kinetic form far into the subsequent cooling period, the "activated" nitrogen not having entirely reverted to its normal condition until at least 0.6 sec. after the end of the combustion period.

#### EXPERIMENTS WITH SOME ISOTHERMIC MIXTURES.

Much confirmatory evidence of the radiant energy-absorbing function and consequent "activation" of nitrogen in the combustion of carbon monoxide at high initial pressures has been obtained as the result of experiments in which mixtures of carbon monoxide and oxygen in their combining proportions, diluted with successive molecular proportions (2, 4, or 6) of the four diluents, argon, carbon monoxide, oxygen, or nitrogen, were fired at such initial pressures as would always result in the liberation of the same total energy (about 10 K.C.U.) during the subsequent explosion. For details of these experiments the reader is referred to the memoir recently published in conjunction with my co-workers (D. M. Newitt and D. T. A. Townend) in the Proceedings of the Royal Society, A. 103, pp. 205-232. There is, however, a significant feature about the

pressure-time records (Fig. 5) obtained when an undiluted  $2CO + O_2$  mixture was fired in our bomb at an initial pressure of 21.4 atmospheres, to which reference should here be made, because of its bearing on the theory of CO-combustion.

It will be seen that the maximum pressure (245 atmospheres) was developed in 0.005 sec., after which the cooling period immediately set in; the pressure fall during the next 0.5 sec. being 66 atmospheres, or about 27 per cent. of the maximum. It is evident that an exceedingly high temperature was momentarily attained in this experiment; indeed, assuming that the

"chemical contraction" involved in the passage from  $2\text{CO} + \text{O}_2$  (3 vols.) to  $2\text{CO}_2$  (2 vols.) was substantially completed at the instant of maximum pressure, the temperature at that instant would have been of the order of  $5000^\circ\text{C}$ . In any case the experiment finally disposes of the supposition that carbon monoxide is inherently a "slow-burning" gas. Moreover, the whole character of the pressure-time curve seems inconsistent with the idea, which has sometimes been put forward, that the maximum pressure attained on explosion is materially affected by the dissociation of carbon dioxide; indeed, there was no sign of any "after burning" or heat evolution after the maximum pressure had been attained.

#### CONCLUDING REMARKS.

The energy of a gaseous system such as we have considered is of course comprised partly of translational motions of its molecules as a whole, and partly of motions of some kind internal to these molecules. The former causes pressure (temperature), but the latter (which according to circumstances may be partly rotational and partly vibrational) produces no external physical effect other than radiation, which originates in high-frequency vibrations within the molecule.

Now in each of our experiments a definite amount of energy (thermally equivalent to about 10 K.C.U.) was liberated by the union of carbon monoxide and oxygen in the bomb. Presumably the greater part of this would appear as increased kinetic energy of the products as a whole (*i.e.* as pressure). The lesser part of the energy liberated in such explosions would manifest itself as "radiation" of wave-lengths characteristic of burning carbon monoxide; *i.e.* of incipiently forming carbon dioxide molecules in a highly vibrating state such as would result from CO and :O collisions. Now when nitrogen is present as a diluent it is able to intercept part of the "radiation" whereby it acquires energy of a vibrational kind, which may be intense enough even to dissociate the two atoms of its molecule, or in any case to "activate" it chemically. Such an absorption of radiant energy presumably would not affect the ratios  $P_m/P_s$ , except in so far as any part of the nitrogen primarily "activated" successfully competed with the burning carbon monoxide for the available oxygen, and thus became oxidised to nitric oxide during the combustion period. Indeed further experiments (now proceeding) have shown that such nitrogen "activation" is materially influenced by the initial pressure at which the explosive mixtures are fired; but this is an aspect of the matter which time does not permit me to develop.

There is of course nothing new in the idea of an "active" form of nitrogen, for ten years ago the Hon. R. J. Strutt (now Lord Rayleigh) discoursed upon it, and showed how ordinary nitrogen is chemically "activated" when subjected at low pressures to a Leyden jar discharge, whereby it glows and acquires the power of combining with various substances towards which it is normally inert. Such "active" nitrogen was found to be strongly endothermic, and Strutt favoured the view that it consists

of dissociated nitrogen atoms, and recombination to form ordinary nitrogen caused the characteristic after-glow.<sup>4</sup>

Another view of the "activation" of nitrogen has been suggested which does not necessitate the complete dissociation of nitrogen molecules. According to Langmuir's statical representation of atomic constitution, there is a great similarity between the configuration of carbon monoxide and nitrogen molecules in the ordinary state, a circumstance to which he has directed special attention. He considers that both molecules are capable of existing in two forms, in one of which (the ordinary and more inert form) the two positive nuclei are both symmetrically located within one and the same outermost shell of eight electrons, whereas in the "active" form they are situated each within one of two separate shells, which have four electrons in common. According to this view not only would the "activation" of each gas be brought about by a reversible transformation from the one configuration into the other, as is shown in Fig. 6, but also an

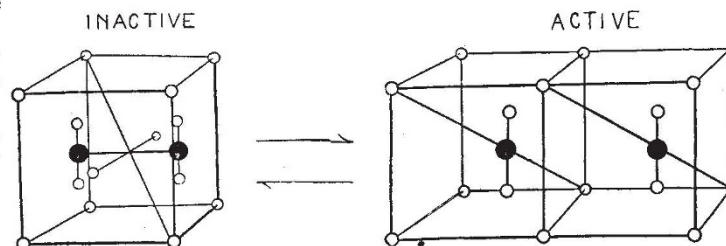


FIG. 6.—Models illustrating the reversible transformation of active nitrogen or carbon monoxide into the inactive form.

inert nitrogen configuration should be capable of being activated through resonance with a carbon monoxide molecule of similar configuration undergoing combustion.<sup>5</sup>

It is interesting now to recall the following passage from one of Faraday's letters to Schönbein, which was quoted by the present Lord Rayleigh, when lecturing on "Active Nitrogen" ten years ago. "What of nitrogen? Is not its apparent quiet simplicity of action all a sham? Not a sham, indeed, but still not the only state in which it can exist. If the compounds which a body can form show something of the state and powers it may have when isolated, then what should nitrogen be in its separate state?" Perhaps the behaviour of nitrogen in our high-pressure carbon monoxide-air explosions will help in realising more fully the deep significance of Faraday's words.

In the earlier part of my discourse I directed attention to the peculiar influence of a small addition of hydrogen to a carbon monoxide-air mixture undergoing combustion whether at atmospheric pressure or when exploded at high pressures in the bomb. We have also found that a similar small addition of hydrogen to a normal carbon monoxide-air mixture

<sup>4</sup> Proc. Roy. Inst., vol. xx, part 3 (1914), pp. 656-6r.

<sup>5</sup> It may be noted that support is given to the idea of a similarity between the electronic configurations of nitrogen and carbon monoxide, and their capability of acting in resonance during explosions at high pressures, by a paper appearing in the Proceedings of the Physico-Mathematical Society of Japan for April last (*vide* NATURE, June 23, p. 859). For if the electronic configurations of the two gases are similar, their band spectra should be in close agreement; and this is shown to be the case. The author, however, remarks that the specific heat ratios of the two gases are incompatible with Langmuir's assumption of the two nuclei being in the same cube; and he suggests an alternative model, in which two cubes are joined at an edge.

undergoing combustion at high pressures is prejudicial to the "activation" of nitrogen. This is a point of considerable theoretical as well as practical interest; and it harmonises with the views which I have put forward respecting the mechanism of carbon monoxide combustion.

Leaving the many theoretical issues raised by our experiments to be settled by a further appeal to facts as the investigation proceeds, I perhaps may be permitted to indicate in conclusion one or two directions in which, if followed up with adequate means and resources, the work might lead to results of further interest.

In the first place, we have already in some of our experiments attained extraordinarily high temperatures; and we could go even higher were it not for the fact that we are approaching the safety limits of the bomb. If funds were forthcoming for the construction of a new bomb, with the necessary accessories, to enable us to work at still higher initial pressures than we have hitherto employed, we should be able to study the effects of subjecting small quantities of diluent gases to the combined influence

of exceedingly high temperatures and intensive radiation. This is an aspect of the research which we are hoping it may be possible for us to pursue in the interests of science.

It is also obvious that our results may have considerable bearing upon the problem of nitrogen fixation. For, having proved that nitrogen can be activated by the combustion of carbon monoxide at high pressures, especially when hydrogen is so far as possible excluded from the system, we have in blast-furnace gas an almost unlimited supply of just the right kind of raw material from which nitric acid could undoubtedly be easily produced under the conditions indicated by our experiment. In view of the national importance of nitrogen fixation we hope these possibilities will be thoroughly explored at home, and not left entirely to foreign organisations, which will probably not be slow to seize upon them. High-pressure combustion work is opening up new possibilities of extending our knowledge, and however much chemical research may have taught us concerning flame and combustion since the time of Davy, there remains a vast amount still to be learned.

### Current Topics and Events.

THE terrible calamity in Japan caused by an earthquake on Saturday last, September 1, arouses the most profound sympathy in the scientific world, in which every one has the highest regard for the brilliant achievements of the Japanese. It is reported that the cities of Yokohama and Tokyo, including the Imperial University buildings, have practically been destroyed and that as many as 300,000 persons have lost their lives. The catastrophe is therefore one of the greatest ever recorded, and Japan will need all the help which other nations can give in order to recover from it. The chief shocks occurred about noon on Saturday and were recorded at 4h. 11m. 18s. on Saturday morning on Mr. J. J. Shaw's seismograph at West Bromwich, Birmingham, as well as at other seismological stations throughout the world. The earthquake was preceded by a typhoon; and it will be remembered that the Messina-Reggio earthquake at the end of 1908, when 77,000 lives were lost, was similarly preceded by torrential rain. It is reported that the Osaka Observatory places the seismic centre in the Izu Peninsula. When, in 1906, an earthquake wrecked a great part of the city of San Francisco, the terrible fire which broke out immediately afterwards completed the destruction, and this appears to have been the course of events at Tokyo and Yokohama. As is usual, high sea-waves, often incorrectly called "tidal waves," have flooded low-lying land and thereby added to the destruction and casualties. Most Japanese earthquakes originate in the great trough of the ocean floor, nearly 5½ miles deep, known as the Tuscarora Deep, between the Kurile Islands and the coast of Japan. This was the place of origin in 1896 when the coast of Japan was devastated by three great waves, the largest about 50 feet in height, which caused the destruction of 20,000 lives in a few minutes. The Messina-Reggio earthquake similarly

originated beneath the sea and a destructive sea-wave rose to a height of 25 feet and swept over the coasts on both sides of Messina Strait. Japan has suffered grievously from earthquakes and effects caused by them, but the catastrophe of Saturday last seems to have been the worst that it has experienced, and the Japanese people will need great fortitude in order to face the future with the confidence in which they have met other trials in the past.

SIR ARTHUR EVANS has published in the *Times* of August 28 and 29 an account of his past season's excavations at Knossos, which have produced some remarkable results. In particular, a wonderful series of frescoes was recovered from a town house, belonging to the beginning of the Late Minoan age, which was found at a depth of about five metres in an unexcavated strip of ground running up almost to the western border of the Palace. The frescoes had been torn from the walls of upper rooms in the house and lay heaped together in a very fragile state. The principal elements of three or four whole scenes, besides a multitude of detailed features, have been reconstituted. Taken as a whole they are said to afford a unique illustration of the painter's art of the golden age of Minoan Crete at approximately 1600 B.C. The variety of naturalistic detail, which is described as going beyond anything yet brought to light among Minoan remains, includes marine growths, birds, and many flowering plants, some of which can be identified. Monkeys of the genus *Cercopithecus*, which are not found nearer than the Sudan, and a group of three warriors, of which two are negro mercenaries, point to close African connexions. Some of the painted fragments are partly filled with Minoan writing. The abutment on the Palace of the important prehistoric main road from the south has been established, and Sir Arthur Evans