

ART. XXXV.—*On a Hypothesis to explain the partial non-explosive Combination of Explosive Gases and Gaseous Mixtures*; by W. G. MIXTER.

[Contributions from the Sheffield Laboratory of Yale University.]

MUCH has been done in investigations of the conditions under which gases combine gradually or with explosive violence. The velocity of explosive waves has been determined, and the influences of pressure, and of excess of one gas or dilution with an indifferent one, have been studied. Dixon\* states, "The explosive wave is propagated not only by burnt molecules, but also by those of the heated but yet unburnt molecules." But so far as the writer is aware, no hypothesis has been advanced to account for the fact that explosive mixtures will not explode at low pressures, and that weak electric sparks may not cause explosions, where strong sparks do. Victor Meyer, with the aid of his pupils, has made a large number of experiments with explosive mixtures at different temperatures and pressures, but he has offered no explanation of the phenomenon of slow combination in such mixtures. As the union of hydrogen and oxygen has been more thoroughly studied than that of other gases, the deportment of detonating gas, by which is understood equivalent amounts of hydrogen and oxygen, under various conditions, affords the best basis for discussion. The behavior of certain other gases, and the observations of different experimenters, will also be considered.

Dixon† found that detonating gas at a pressure of 70<sup>mm</sup> does not explode when an electric spark is passed through it, and

\* Chem. News, lxxvii, 39.

† Trans. Roy. Soc., 1884, 634.

L. Meyer and Seubert\* observed at the same pressure that three-fourths of the gas combined. The writer noticed† that weak sparks did not cause an explosion of the gas. This is not peculiar to detonating gas, as Dixon‡ states that "The explosion of cyanogen and oxygen depends solely on the nature of the spark. A strong spark causes the mixture to explode violently, whether wet or dry. A weak spark may be passed through the mixture, wet or dry, without apparent effect."

Emich§ has recently studied the inflammability of thin layers of explosive mixtures of gases, and has found that the length of the spark required for ignition bears an inverse relation to the density, and that the addition of oxygen to detonating gas till it is to the hydrogen as 1:1 increased the sensitiveness of the mixture to sparks; an analogous fact obtains for an explosive mixture of hydrogen and chlorine. On the contrary, equivalent mixtures of carbonic oxide and oxygen are more sensitive than those containing an excess of either.

The glow discharge of electricity produces gradual combination of explosive mixtures.¶ Meyer and Raum¶ experimented with detonating gas in sealed bulbs, and observed no perceptible combination after exposure for 218 days, to a temperature of 100°, while after 65 days, at 300°, they found in three tests that 9.5, 0.4, and 1.3 per cent of the gas had united. They obtained at 350° and 50 hours, 1.6 per cent, and after 120 hours, 1.9, 16.4, 0.5, 0.7 per cent. Krause and Meyer\*\* found that 28 to 100 per cent of detonating gas combined when heated to 518° for 2 hours, in sealed bulbs. On the other hand, Askenasy and Meyer†† observed that but little water was formed where the gas passed slowly through a vessel at 606°. Freyer and Meyer‡‡ determined the temperatures at which mixtures of gases exploded when slowly passing through a hot vessel, and also when quickly heated in sealed bulbs. Explosions occurred at the higher temperatures given in the following table, but not at the lower:

		With free current.	In sealed bulbs.
Hydrogen	} with oxygen required for complete combustion	650–730°	518–606°
Methane		650–730°	606–650°
Ethane		606–650°	518–606°
Ethylane		606–650°	518–606°
Carbonic oxide		650–730°	650–730°
Hydrogen sulphide		315–320°	250–270°
Hydrogen and Chlorine		430–440°	240–270°

\* Jour. Chem. Soc., xlv, 587.

† J. Chem. Soc., xlix, 384.

‡ This Journal, iv, 51, 1897.

\*\* Liebig's Ann., cclxiv, 85.

† This Journal, iv, 51.

§ Monatsheft f. Chem., xviii, 6, xix, 299.

¶ Ber. d. deutsch. Gesell., xxviii, 2804.

†† Liebig's Ann., cclxix, 49.

‡‡ Zeitschr. für phys. Chem., xi, 28.

They also found that detonating gas suddenly heated in unsealed bulbs exploded at the same temperature as in sealed.

Before discussing chemical changes let us recall the condition of matter in gases—the molecules are moving very rapidly, some faster, some slower, an individual molecule moving in a straight line for a very short distance, until it strikes another. These collisions of one molecule with others are very frequent. The atoms composing a molecule are also moving in respect to each other, this motion constituting a portion of the internal energy of the molecules, which is continually diminishing through radiation. When the gas is heated the mean velocity of the molecules is increased, and at the same time the atomic motion and internal energy are also increased. At a sufficiently high temperature some of the collisions are so violent as to disrupt the molecules and their atoms part company.

When a mixture of gases is heated, chemical combination results from the encounters of different kinds of molecules having motion of translation, or of the atoms, or of both. At any given temperature the mean velocity of molecules may be calculated, but we have no data for determining at what greater velocity the molecular collisions are followed by chemical union. Polyatomic molecules are dissociated by heat, but since there is no measurable dissociation of hydrogen or oxygen at 1600° it does not appear that dissociation by heat plays much part in the change. Whatever the chemical changes caused by heat in gases, whether combination or dissociation, the condition necessary for these changes results from molecular impacts. If, for example, detonating gas be heated, a part of the molecules acquire a velocity and internal energy adequate for combination. Some of these encounter each other and combine to form water, the free atoms of oxygen uniting with each other or with hydrogen. The nascent water molecules have in general a high velocity, and collide with those of oxygen and hydrogen; but it is not probable that a single impact of a new water molecule with one of hydrogen or oxygen imparts to the latter energy adequate for combination. If it were so, the change would proceed with accelerating speed at a temperature of 300° to 500°. This view, that a nascent water molecule does not necessarily cause hydrogen and oxygen to unite, accords with that expressed by the writer,\* that the heat of combination caused by the glow discharge of electricity does not produce further combination.

Why is it that chemical union proceeds slowly at 500°, and why does not the energy resulting from combination cause further combination, and thus raise the temperature of the sys-

\* This Journal, vi, 218, 1898.

tem to the point of explosion? Let us suppose the mixed gases be heated from  $500^{\circ}$  to  $501^{\circ}$ . This increase in temperature will not cause them to explode. Assume further, that the heat of combustion during one minute is sufficient to raise the temperature of the gases  $1^{\circ}$ , provided no heat is lost by radiation. Experiments have shown that this rise in temperature will not cause explosion. But the gases heated by their own slow combustion continually lose heat by radiation, and hence are only slightly hotter than the surrounding medium. Were it possible to prevent loss of heat, the temperature would rise and the change proceed with accelerating speed.

The observations of Freyer and Meyer (*loc. cit.*), that explosive mixtures gradually heated have a higher ignition point than when suddenly heated, are difficult to explain, and further experiments may be useful. Their results also indicate that pressure is without influence, while A. Mitscherlich\* found that at pressures less than one atmosphere the ignition point falls with the pressure. As pressure in so many cases influences explosion, it is remarkable in Freyer and Meyer's experiments that detonating gas in an open vessel, when quickly heated, exploded at the same temperature as it did under a pressure of two atmospheres or more. Mitscherlich's results also are the opposite of what we might expect.

Let us first consider the phenomenon of explosion of detonating gas at a low pressure when the combination is not complete. An electric spark or hot wire ignites the gas, the water molecules about the source of heat collide with the neighboring ones of hydrogen and oxygen, molecules of these elements being shaken up by many impacts and acquiring energy adequate for combination, and thus uniting and adding energy to the system. In this way the change propagates itself. A part of the molecules of hydrogen and oxygen have not combined. Why? When a denser gas is ignited, the combination is complete, and as the temperature of burning hydrogen is sufficient to dissociate water, we must assume that some of the water molecules are broken up, and as the temperature falls they reform, all of the hydrogen and oxygen uniting before the temperature is too low for combination. In the case of the rarer gas, the impacts to which a molecule of hydrogen or oxygen is subject from the nascent water molecules are less frequent than in the denser gas, and hence it is not as likely to acquire the energy needed for chemical union. Moreover, molecules possessing velocities adequate for combination encounter each other less frequently in the rare gas; hence the chemical change will proceed more slowly, and there will be more time for the system to lose heat by radiation. A

\* Ber. d. deutsch. Chem. Gesell., xxvi, 399.

molecule with internal energy adequate for combination loses this energy if its free path is relatively long; that is, given sufficient time though very brief, the molecule assumes a condition unfavorable to chemical union.

Let us now see if other phenomena are explained by this hypothesis, considering first the case of an electric spark in detonating gas at a pressure too low for explosion. Here we have an enormous number of molecules combining in the luminous path of the spark. These radiate energy, part being electrical in its origin, i. e., a portion which was derived from the external work done upon the gas, and part resulting from chemical union. These encounter neighboring molecules of hydrogen and oxygen, imparting to some of them energy adequate for combination. Of these last a part combine, and we have now to consider a portion of gas consisting of water molecules, as well as those of hydrogen and oxygen. Some of the last named possess energy adequate for chemical union, but their encounters are too infrequent to restore by the heat of combination the energy radiated, hence the change proceeds with diminishing speed and finally ceases to propagate itself.

Feeble sparks do not explode detonating gas at a pressure of half an atmosphere or even more, but they cause slow combination. In this case it is not necessary to consider the possibility of the hydrogen carrying the electricity, since water molecules are formed, and we need only take into account a system made up of a relatively small number of nascent molecules of water, molecules of hydrogen and oxygen having energy adequate for combination, together with a relatively large number of molecules of these gases not having such energy. Under these conditions the impacts resulting in chemical union are too infrequent to maintain by the heat of their combustion the energy lost by radiation, and consequently the change does not propagate itself and cause an explosion.

Carbonic oxide and oxygen combine slowly at pressures less than an atmosphere when subjected to feeble sparks. Here too the impacts of molecules with a velocity adequate for chemical union are infrequent, as is evident from the fact that the change does not propagate itself.

In the case of cyanogen and oxygen either the feeble spark causes no chemical union, which is improbable, or as in the previous instances the change does not proceed throughout the gas because of the infrequency of impacts of high velocity molecules.

The study of the phenomena of explosives involves the thermal effect, but for the present purpose the heat evolved by the explosion or decomposition of equal volumes will suffice.

Two grams and 2 volumes of hydrogen burn with 1 volume of oxygen, with a thermal result of 58,700 calories, the product gaseous; and 2 volumes of the mixture, therefore, give 39,134 c. Likewise, 2 volumes of carbonic oxide and oxygen give 45,312 c.; 1 volume of hydrogen and 1 of chlorine give 22,000 c.; and 24 grams of solid carbon and 2 of hydrogen unite with an absorption of 48,170 c. to form 2 volumes of acetylene, which evolves this amount of heat when resolved into its elements. In the same way, we have for cyanogen 65,700 c., for nitrous oxide 17,470 c., and for nitric oxide 21,575 c. set free when these compounds are decomposed into their elements. The following table gives the resultant heat of the combination of equal volumes of three mixtures, and of the decomposition of four endothermic gases:

	Resultant heat.	Nature of product.
Hydrogen and oxygen .....	39134	Gaseous
Hydrogen and chlorine .....	22000	"
Carbonic oxide and oxygen..	45312	"
Acetylene .....	48170	12/13 solid
Cyanogen .....	65700	12/21 "
Nitrous oxide .....	17470	Gaseous
Nitric oxide .....	21575	"

The molecular heats at constant volume of  $H_2$ ,  $O_2$ ,  $N_2$ ,  $CO$ ,  $NO$ , and  $HCl$  are 4.2 to 5, and of  $N_2O$ ,  $H_2O$ , and  $CO_2$ , about one-half larger. Those of  $C_2H_2$  and  $C_2N_2$  do not appear to have been determined, but they are probably not greater than 10. Evidently the molecular heats have little influence in determining the temperature at which explosion occurs, and the resultant heat does not account for the fact that the ignition temperature of chlorine and hydrogen is much lower than that of hydrogen and oxygen, or of carbonic oxide and oxygen.

Acetylene requires a pressure 20 times greater than detonating gas for explosion, while the heat of decomposition of the former exceeds that of chemical union of the latter. At temperatures not high enough to cause acetylene to separate completely into its elements or cause detonating gas to explode, the two gases exhibit similar deportment in this respect, namely, that the change is one of slow combination. Acetylene polymerizes to form  $C_6H_6$ ,  $C_8H_8$ , and other condensation products, and detonating gas forms water. But acetylene, when sparked under sufficient pressure, decomposes completely into carbon and hydrogen. The impacts of acetylene molecules with a certain velocity causes them to combine with each other, but when they have a higher velocity complete decomposition results. The change started by a spark in dense acety-

lene propagates itself throughout the gas. About the path of the spark there are sufficiently numerous encounters of molecules with a velocity adequate to cause decomposition, and the heat resulting is not lost by radiation before other molecules of acetylene are decomposed. Thus the change continues until only solid carbon and stable molecules of hydrogen remain. A proposed method for the commercial production of lampblack depends upon this fact. When, however, a spark passes through the gas at common pressure, the change occurs only in the path of the spark. Here the impacts of molecules with a velocity adequate to cause decomposition are more infrequent than in the denser gas—too infrequent, as the result shows, to propagate the change. The heat about the path of the spark is dissipated by radiation before it decomposes neighboring molecules. The infrequency of impacts allows sufficient time for radiation, and for the molecules to assume a stable condition. It is also probable that some more stable molecules, such as  $C_6H_6$ , are formed. If acetylene issuing from a tube is lighted, the decomposition does not extend into the tube for the same reason that it does not extend through the gas when sparked at ordinary pressure.

The deportment of acetylene under high pressure, when subjected to small sparks (p. 324) is similar to that of detonating gas.\* Condensation products are formed in one case and water in the other. The minute spark imparts to the molecules of acetylene energy adequate to effect combination, and as the spark is visible we assume that the portion of the gas which is glowing has a temperature at which acetylene decomposes when larger quantities are heated. Thus the infrequency of impacts of molecules of high velocity is the real reason why feeble sparks do not start an explosion in dense acetylene.

The non-explosion of cyanogen (p. 325) under high pressure when sparked, although it is more endothermic than acetylene; is doubtless connected with the fact that it requires a higher temperature for its decomposition than the latter; or it may be that the union of CN with CN is exothermic, while the radical itself is endothermic. Nitrous oxide and nitric oxide are stable at high temperatures and these also do not decompose with explosive violence when sparked under pressure. It is probable that all three of these endothermic gases would explode if sparked under pressure and at a temperature approaching that at which they dissociate.

\* This Journal, iv, 51.

*Recapitulation.*

Detonating gas, a mixture of carbonic oxide and oxygen, one of cyanogen and oxygen, and other explosive mixtures of gases do not explode below certain pressures when sparked: and the decomposition of acetylene does not propagate itself at pressures less than two atmospheres. In the path of the spark chemical changes occur which do not extend throughout the gases, and the same is true of a weak spark in the gases mentioned when under a pressure at which a strong spark explodes them. It appears for reasons already stated that explosions do not occur in the instances given only because of the infrequency of impacts of molecules having a velocity or internal energy adequate for chemical union. In the rare gas the impacts are less frequent than in a dense gas, the mean free path is longer, and there is more time for a molecule with energy adequate for combination to lose this energy by radiation and to attain a condition unfavorable to chemical union. Some of the molecules combine, but the heat of their union is not sufficient to restore the energy lost by radiation and the change is therefore not self-propagating. The same explanation holds good for the phenomena of feeble sparks in a dense explosive gas where in the path of a spark there are relatively few molecules with energy adequate for combination, and these collide with each other less frequently than with the molecules not having such energy. In a dense gas a given quantity and a degree of heat, that is, sufficient frequency of molecular impacts, is requisite to secure spontaneous extension of the change.