Company at their Foyers works, alumina, of which the melting-point is certainly above $1700^{\circ} \mathrm{C}$. or $1800^{\circ} \mathrm{C}$., is dissolved in a bath of melted cryolite at a temperature of about $800^{\circ} \mathrm{C}$. So we may imagine melted basalt to be a solvent for felspar, hornblende, mica, and quartz at temperatures much below their own separate melting-points; and we can understand how the basaltic rocks of the earth may have resulted from the solidification of the mother liquor from which the crystalline ingredients of granite have been deposited.

VI. On the Rate of Explosion in Gases.<br>By D. L. Chapman, B.A. (Oxon.)*.

THE object of the investigation of which an account is given in this paper is the discovery of formule to express the maximum rates of explosion in gases and the maximam pressure in the explosive wave.

The dala which I propose to use are taken almost entirely from the Bakerian Lecture of 1893, on "The Rates of Explosion in Gases," by Prof. Dixon. The maximum velocities of explosion given below are in all cases those measured by Prof. Dixon or under his direction. Experimental conclusions only will be quoted; for a complete account of the experiments themselves, the reader is referred to the above-mentioned paper, and to several papers which were subsequently published in the 'Journal of the Manchester Literary and Philosophical Society' and in the 'Journal of the Chemical Society.'

Ignoring for the present all minor details connected with particular cases, which may be more conveniently discussed at a later stage, it is sufficient for our purpose to state at the ontset that it has been established that the maximum velocity of explosion, in a mixture of definite composition and at fixed temperature and pressure, has a definite value, independent of the diameter of the tube when that diameter exceeds a certain limit. The relations existing between temperature and pressure and the velocity of explosion are such that an increase of temperature causes a fall in the velocity, whereas an increase of pressure has the reverse effect up to a certain limit, beyond which the velocity remains constant.

For the suggestion that an explosion is in its character essentially similar to a sound-wave, we are also indebted to Prof. Dixon ; and there is little doubt that all subsequent advance must be made with this suggestion as the leading

[^0]idea *. Although Prof. Dixon's sound-wave formula has yielded such excellent results, he has pointed out the necessity of further $\dot{a}$ priori work in the subject.

## The Rate of Explosion for an Infinite Plane Wave.

In the following attempt to establish a formula for the velocity of explosion, 1 have made certain assumptions which have not as yet received sufficient experimental confirmation ; but they are. I think, justified by the results. For instance, it is assumed that, once the maximum velocity is reached, the front of the explosion wave is of such a character that we may suppose steady motion. This, as Prof. Schuster has pointed out in a note to the Bakerian Lecture, is not an impossibility when chemical change is taking place, since the implied relation between pressure and density is possible under such circumstances. This point, however, requires further investigation. The wave is assumed to be an infinite plane wave. This assumption is justified by the fact that the diameter of the tube is without influence on the found velocity. I propose to limit the term " explosive wave" to the space within which chemical change is taking place. This space is bounded by two infinite planes. On either side of the wave are the exploded and unexploded gases, which are assumed to have uniform densities and velocities. The statement that the exploded gas possesses uniform density and velocity for some distance behind the wave requires further justification, which can only be imperfectly given after a discussion of the general problem.

How the true explosive wave is actually generated in practice is a question without the scope of the present investigation. In order to avoid the discussion of this point, I shall substitute for it a physical conception, which, although unrealizable in practice, will render aid in illustrating the views here advanced.

Let us suppose that the gas is enclosed in an infinite cylinder ABCD, provided with a piston E, and that the explosive wave XYZS has just started. The initial velocity of this wave will be small; the initial pressure along the plane XS will also be small compared with that ultimately attained. As the wave proceeds in the direction $A B$, the piston E is supposed to follow it in such a manner that

[^1]the pressure at EF is always kept equal to the pressure at XS. During this process the velocity of the wave will gradually increase, until ultimately its velocity will be uniform, its type constant, and the exploded gas within the area EXSF homogeneous. It is this ultimate steady

Fig. 1.

state alone which I propose to consider. During the process just described the velocity will of course constantly increase until it attains a maximum. After the velocity has become uniform, and the wave permanent in type, it is obvious that another permanent state may be reached in the following way :-Suppose a piston is introduced immediately behind the permanent wave, and that this piston is made to move forward more rapidly than the previous one, the pressure and density behind the wave will thus be increased, and after a certain period of time another steady state will be reached. All this is equivalent to the statement that the permanent velocity of explosion is a function of the density of the exploded gas.

I shall now proceed to prove the latter statement.
Since the discussion is limited to the wave of permanent type, we may write down the condition of steady motion,

$$
\begin{equation*}
\frac{u}{v}=\frac{\mathrm{V}}{v_{0}}, \tag{1}
\end{equation*}
$$

where V and ${ }^{\circ} u$ are the velocities of the unexploded and exploded gas respectively, referred to coordinates moving with a velocity -V , and $v_{0}$ and $v$ are the volumes of a gramequivalent of the unexploded and exploded gas.

Take as an example cyanogen and oxygen, the explosion of which is represented by the equation

$$
\begin{aligned}
\mathrm{C}_{2} \mathrm{~N}_{2}+\mathrm{O}_{2} & =2 \mathrm{CO}+\mathrm{N}_{2} \\
22 \cdot 4 \text { litres }+22 \cdot 4 \text { litres } & =44 \cdot 8 \text { litres }+22 \cdot 4 \text { litres. } \\
52 \text { grms. }+32 \text { grms. } & =56 \text { grms. }+28 \text { grms. }
\end{aligned}
$$

Here $v_{0}=44 \cdot 8$ litres, and $v$ is the volume of carbon monoxide
and nitrogen obtained from this immediately after the explosion.

$$
\mu=\text { gram-equivalent (in this case, } 84 \text { grms.). }
$$

From (1) and the equations of motion, we obtain

$$
p-p_{0}=\frac{\mu \mathrm{V}^{2}}{v_{0}^{2}}\left(v_{0}-v\right) . \quad . \quad . \quad \cdot(2)^{*}
$$

This formula of Riemann assumes a relation to subsist between $\mathrm{V}, p$, and $v$ at all points of the wave; and from it the work performed by the wave during explosion may be calculated.

Work performed by the gas

$$
\begin{aligned}
=\int_{v_{0}}^{v} p d v & =\frac{\mu \mathrm{V}^{2}}{v_{0}} \int_{v_{0}}^{v}\left(v_{0}-v\right) d v+\int_{v_{0}}^{v} p_{0} d v \\
& =-\frac{\mu \mathrm{V}^{2}}{2 v_{0}}\left(v-v_{0}\right)^{2}+p_{0}\left(v-v_{0}\right)
\end{aligned}
$$

For the purpose of testing this result, it may be shown that the external work performed by the piston (fig. 1) is equal to the work performed on the gas together with the gain of kinetic energy.

The work performed on the gas

$$
=\frac{\mu \mathrm{V}^{2}}{2 v_{0}^{2}}\left(v-v_{0}\right)^{2}+p_{0}\left(v_{0}-v\right) .
$$

The gain of kinetic energy

$$
\begin{aligned}
& =\frac{(\mathrm{V}-u)^{2} \mu}{2} \\
& =\frac{\mu \mathrm{V}^{2}}{2 v_{0}^{2}}\left(v_{0}-v\right)^{2}, \quad \text { since } u=\frac{\mathrm{V} v}{v_{0}} .
\end{aligned}
$$

The external work performed by the piston

$$
\begin{aligned}
& =p\left(v_{0}-v\right) \\
& =\frac{\mu \mathrm{V}^{2}}{v_{0}{ }^{2}}\left(v_{0}-v\right)^{2}+p_{0}\left(v_{0}-v\right) .
\end{aligned}
$$

$\therefore$ External work performed by the piston
= gain of kinetic energy + work performed on the gas.
Assume that in the explosion $n$ molecules become $m$ molecules. For example, in the explosion of equal volumes of

* Rayleigh's • Sound,' vol. ii. ; Schuster's note in the Bakerian Lecture on Explosions.
cyanogen and oxygen, $n$ is 2 and $m$ is 3 :

$$
\underset{(2 \text { molecules })}{\mathrm{C}_{2} \mathrm{~N}_{2}+\mathrm{O}_{2}}=\underset{(3 \text { molecules })}{2 \mathrm{CO}+\mathrm{N}_{Q} .}
$$

I shall now calculate the energy lost when a gas is allowed to burn and the products of combustion are collected at the normal temperature and pressure.

Assume that one of the gases is enclosed in the cylinder A and the other in the cylinder B (fig. 2). These gases are forced

Fig. 2.

out, burned at C , cooled at D , and collected in the cylinder E . The gain of energy is the work performed by the pistons $a$ and $b$; and the loss of energy is the heat evolved at D , together with the work performed on the piston $e$. The total energy lost is the difference of these. The volume of gas in A and B is $x_{0}$; therefore the work performed by the pistons $a$ and $b$ is $p_{0} v_{0}$. The volume of burnt gas is $\frac{m v_{0}}{n}$; and therefore the work performed on the piston $e$ is $\frac{m p_{0} y_{0}}{n}$.

The heat evolved at $D$ is the heat of combustion at constant pressure ; call it $h$. Let the total energy lost $=\mathrm{II}$.

Then

$$
\mathrm{H}=h+p_{0} v_{0}\left(\frac{m}{n}-1\right) .
$$

During an explosion the whole of this energy is retained by the gas, and in addition to this it gains an amount of energy equal to the work performed on the gas.
The energy of the exploded gas is therefore given by the expression

$$
\begin{aligned}
h+p_{0} v_{0}\left(\frac{m}{n}-1\right)+\frac{\mu \mathrm{V}^{2}}{2 v_{0}^{2}}\left(v-v_{0}\right)^{2}-p_{0}\left(v-v_{0}\right) \\
+ \text { energy of exploded gas at } \mathrm{N} .
\end{aligned} \quad \begin{aligned}
& \quad=h+\frac{\mu \mathrm{V}^{2}}{2 v_{0}^{2}}\left(v-v_{0}\right)^{2}-p_{0} v+p_{0} v_{0} \frac{m}{n}+\text { energy at N.T.P. }
\end{aligned}
$$

If $t_{0}$ is the normal temperature, and $t$ the temperature of the gas after explosion,

$$
\begin{align*}
& m \mathrm{C}_{v}\left(t-t_{0}\right)+\text { energy at N.T.P.=energy of exploded gas; } \\
& \therefore \quad m \mathrm{C}_{v}\left(t-t_{0}\right)=h+\frac{\mu \mathrm{V}^{2}}{2 v_{0}^{2}}\left(v-v_{0}\right)^{2}-p_{0} v+p_{0} v_{0} \frac{m}{n} ; \\
& \therefore \quad t=\frac{h+\frac{\mu \mathrm{V}^{2}}{2 v_{0}^{2}}\left(v-v_{0}\right)^{2}-p_{0} v+p_{0} v_{0} \frac{m}{n}}{m \mathrm{C}_{v}}+t_{0} . \tag{3}
\end{align*}
$$

Bat $p v=m \mathrm{R} t$,

$$
\therefore \quad p v=\frac{\mathrm{R}}{\mathrm{C}_{v}}\left\{h+\frac{\mu \mathrm{V}^{2}}{2 v_{0}^{2}}\left(v-v_{0}\right)^{2}-p_{0} v+p_{0} v_{0} \frac{m}{n}\right\}+m \mathrm{R} t_{0} .
$$

Also, from equation (2), we get

$$
p v=\frac{\mu \mathrm{V}^{2}}{v_{0}^{2}}\left(v_{0}-v\right) v+p_{0} v ;
$$

$$
\begin{align*}
\therefore \frac{\mathrm{R}}{\mathrm{C}_{v}}\left\{h+\frac{\mu \mathrm{V}^{2}}{2 v_{0}^{2}}\left(v-v_{0}\right)^{2}-p_{0} v\right. & \left.+p_{0} v_{0} \frac{m}{n}\right\}+m \mathrm{R} t_{0} \\
& =\frac{\mu \mathrm{V}^{2}}{v_{0}^{2}}\left(v_{0}-v\right) v+p_{0} v . \tag{4}
\end{align*}
$$

This establishes a relation between V and $v$. The velocity of a permanent explosion is therefore a function of the density of the exploded gas.

When an explosion starts its character and velocity are continually changing until it becomes a wave permanent in type and of uniform velocity. I think it is reasonable to assume that this wave-i:e. the wave of which the velocity has been measured by Prof. Dixon-is that steady wave which possesses minimum velocity ; for, once it has become a permanent wave with uniform velocity, no reason can be discovered for its changing to another permanent wave having a greater uniform velocity and a greater maximum pressure.

This particular velocity may be discovered by eliminating $v$ from the equations
and

$$
\begin{aligned}
& \mathrm{V}=f(v) \\
& 0=\frac{d V}{d v}
\end{aligned}
$$

It may be well to point out that under these circumstances the entropy of the exploded gas is a maximum. This may be easily shown thus :-

The condition for maximum entropy is

$$
\begin{aligned}
0=d \phi & =m \mathrm{C}_{v} \frac{d t}{t}+\frac{p}{t} d v ; \\
\therefore \quad m \mathrm{C}_{v} d t & =-p d v,
\end{aligned}
$$

or

$$
\frac{d t}{d v}=-\frac{p}{m \mathrm{U}_{v}}
$$

By differentiating (3),

$$
\frac{d t}{d v}=\frac{1}{m \mathrm{C}_{v}}\left\{\frac{\mu \mathrm{~V}}{v_{0}^{2}}\left(v-v_{0}\right)^{2} \frac{d \mathrm{~V}}{d v}+\frac{\mu \mathrm{V}^{2}}{v_{0}^{2}}\left(v-v_{0}\right)-p_{0}\right\} ;
$$

but from ( $\alpha$ ) and Riemann's equation

$$
\begin{aligned}
\quad \frac{d t}{d v} & =-\frac{1}{m \mathrm{C}_{v}}\left\{\frac{\mu \mathrm{~V}^{2}}{v_{0}}\left(v_{0}-v\right)+p_{0}\right\} ; \\
\therefore \quad & \frac{d \mathrm{~V}}{d v}=0 ;
\end{aligned}
$$

therefore the condition of minimum velocity is equivalent to the condition of maxinum entropy*.

The following method of arriving at the approximation $v=\frac{\mathrm{C} p}{\mathrm{C} p+\mathrm{C}_{v}} v_{0}$ was suggested by Prof. Schuster, who has shown that the method by which I arrived at the same result is inconclusive.

Equation (4) arranged ${ }^{-}$differently runs

$$
\frac{\mathrm{R} \mu \mathrm{~V}^{2}\left(v-v_{0}\right)^{2}}{2 \mathrm{C}_{v} v_{0}^{2}}+\frac{\mu \mathrm{V}^{2}}{v_{0}{ }^{2}}\left(v-v_{0}\right) v=p_{0} v\left[1+\frac{\mathrm{R}}{\mathrm{C}_{v}}\right]-\mathrm{H},
$$

where H does not contain $v$.
Or putting $\mathrm{R}=\mathrm{C}_{p}-\mathrm{C}_{v}$,

$$
\begin{aligned}
& \frac{\mu \mathrm{V}^{2}\left(v-v_{0}\right)}{v_{0}^{2}}\left[\frac{\mathrm{C}_{p}-\mathrm{C}_{v}}{2 \mathrm{C}_{v}}\left(v-v_{0}\right)+v\right]=p_{0} v \frac{\mathrm{C}_{p}}{\mathrm{C}_{v}}-\mathrm{H} ; \\
\therefore \quad & \frac{\mu \mathrm{V}^{2}}{v_{0}^{2}}=\frac{\mathrm{H}-p_{0} v \mathrm{C}_{p}}{\left(v-v_{0}\right)\left[\frac{\mathrm{C}_{p}-\mathrm{C}_{v}}{2 \mathrm{C}_{v}} v_{0}-\frac{\mathrm{C}_{p}+\mathrm{C}_{v}}{2 \mathrm{C}_{v}} v\right]} .
\end{aligned}
$$

The complete expression $\frac{d V}{d v}=0$ leads to a quadratic expression for $v$. Hence there are two minima or maxima.

* In any adiabatic change the entropy cannot decrease, and therefore it tends to become a maximum,

If

$$
\begin{array}{ll}
v=v_{0}, & \mathrm{~V}^{2}=\infty, \\
v=\frac{\mathrm{C}_{p}-\mathrm{C}_{v}}{\mathrm{C}_{p}+\mathrm{C}_{v}} v_{0}, & \mathrm{~V}^{2}=\infty .
\end{array}
$$

Hence one minimum lies between these values*.
If H is large compared to $p_{0} v \frac{\mathrm{C}_{p}}{\mathrm{C}_{g}}, \mathrm{~V}$ will be a minimum or maximum when

$$
\left(v-v_{0}\right)\left[\frac{\mathrm{C}_{p}-\mathrm{C}_{v}}{2 \mathrm{C}_{v}} v_{0}-\frac{\mathrm{C}_{p}+\mathrm{C}_{v}}{2 \mathrm{C}_{v}} v\right]
$$

is a maximum or minimum.
Writing this F: F will be zero for

$$
\begin{aligned}
& v=v_{0}, \\
& v=\frac{\mathrm{C}_{p}-\mathrm{C}_{v}}{\mathrm{C}_{p}+\mathrm{C}_{v}} v_{0} .
\end{aligned}
$$

For $v= \pm \infty$ it will be negative ; hence between the above values of $v$ there will be a maximum of F or a minimum of V .

Also

$$
\begin{aligned}
2 \mathrm{C}_{v} \frac{d \mathrm{~F}}{d v} & =\left(\mathrm{C}_{p}-\mathrm{C}_{v}\right) \dot{v}_{0}-\left(\mathrm{C}_{p}+\mathrm{C}\right) v-\left(v-v_{0}\right)\left(\mathrm{C}_{p}+\mathrm{C}_{v}\right) \\
& =2 \mathrm{C}_{p} v_{0}-2\left(\mathrm{C}_{p}+\mathrm{C}_{v}\right) v .
\end{aligned}
$$

And $\frac{d^{2} \mathrm{~F}}{d v^{2}}$ is always negative; hence F must be a maximum when

$$
\begin{equation*}
v=\frac{\mathrm{C}_{p}}{\mathrm{C}_{p}+\mathrm{C}_{v}} v_{0} . \quad . \quad . \quad . \tag{5}
\end{equation*}
$$

By eliminating $v$ from (4) and (5) we obtain the value of $\mathrm{V}^{2}$. This elimination leads to the result

$$
\begin{aligned}
\mathrm{V}^{2} & =\frac{2 p_{0} v_{0} \mathrm{C}_{p}}{n \mu \mathrm{C}_{v}^{2}}\left\{(m-n) \mathrm{C}_{p}+m \mathrm{C}_{v}\right\}+\frac{2\left(\mathrm{C}_{p}+\mathrm{C}_{v}\right) \mathrm{R} h}{\mu \mathrm{C}_{v}^{2}} \\
& =\frac{2 \mathrm{R}}{\mu \mathrm{C}_{v}^{2}}\left[\left\{(m-n) \mathrm{C}_{p}+m \mathrm{C}_{v}\right\} \mathrm{C}_{p} t_{0}+\left(\mathrm{C}_{p}+\mathrm{C}_{v}\right) / l\right], \\
\text { since } p_{0} v_{0} & =n \mathrm{R} t_{0} .
\end{aligned}
$$

It is assumed throughout that the exploded gas behind the wave remains at constant temperature and pressure, and has
*The other value of $v$ obtained from the quadratic equation $\frac{d \mathrm{~V}}{d v}=0$ is much larger than $v_{0}$, and gives to $V$ a very small value. It has therefore no connexion with the wave we are considering.

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a uniform velocity. Therefore during the explosion momentum is generated by the moving piston. In an actual explosion in a tube not provided with a piston the whole mass of gas cannot move forward with this uniform velocity, for there would then be a vacuum at the end of the tube where the explosion started, and the pressure at that end would be zero, making it impossible to account for the generation of momentum. There is, howtver, no need to assume that the whole exploded gas acquires a uniform velocity. In fact the velocity of the wave would be the same if it were followed by a layer of exploded gas of uniform density and velocity, and would be unaffected by any subsequent disturbance which must take place behind the explosive wave.

It is therefore necessary to prove that behind the explosive wave there is a layer of homogeneous gas. This evidently must be if any disturbance behind the wave can only move forward with a velocity less than that of the wave itself.

The forward velocity of any disturbance in the exploded gas will be given by the sum of the velocity of the gas and the velocity of sound in the gas.

The velocity of the gas

$$
\begin{aligned}
=\mathrm{V}-u & =\mathrm{V}\left(1-\frac{v}{v_{0}}\right) \\
& =\mathrm{V}\left(\frac{\mathrm{C}_{v}}{\mathrm{O}_{p}+\mathrm{C}_{v}}\right) .
\end{aligned}
$$

The velocity of sound

$$
=\sqrt{\frac{m \mathrm{H} t}{\mu} \frac{\mathrm{C}_{p}}{\mathrm{C}_{v}}} .
$$

In the complete expression for $\mathrm{V}^{2}$ the first term may be here neglected. Also in the complete expression for $t$ (equation (3)) the last three terms are small. We may therefore write

$$
\mathrm{V}^{2} \bumpeq \frac{2 \mathrm{R}\left(\mathrm{C}_{p}+\mathrm{C}_{v}\right) h}{\mu \mathrm{C}_{v}{ }^{2}},
$$

and

$$
t \bumpeq \frac{h+\frac{\mu V^{2}}{2 v_{0}^{2}}\left(v-v_{0}\right)^{2}}{m \mathrm{C}} .
$$

Employing these values, the velocity of the gas becomes

$$
\sqrt{\frac{2 \mathrm{R} h}{\mu}\left(\frac{1}{\mathrm{C}_{p}+\mathrm{C}}\right)},
$$

and the velocity of sound

$$
\sqrt{\frac{2 \mathrm{R} /}{\mu}\left(\frac{\mathrm{U}_{p}^{2}}{\mathrm{C}_{v}^{2}\left(\mathrm{C}_{p}+\mathrm{C}_{v}\right)}\right)} ;
$$

$\therefore$ the velocity or sound + velocity of the gas

$$
=\sqrt{\frac{2 \mathrm{R} h}{\mu} \cdot \frac{\mathrm{C}_{p}^{2}+\mathrm{C}_{v}^{2}}{\mathrm{C}_{v}^{2}\left(\mathrm{C}_{p}+\mathrm{C}_{v}\right)}}
$$

The velocity of explosion

$$
=\sqrt{\frac{2 \mathrm{R} / h}{\mu} \frac{\left(\mathrm{C}_{p}+\mathrm{C}_{v}\right)^{2}}{\mathrm{C}_{v}^{2}\left(\mathrm{C}_{p}+\mathrm{C}_{v}\right)}} .
$$

The latter is evidently greater than the former. Therefore the layer of uniform gas behind the wave will gradually become greater as the explosion proceeds.

## Calculation of the Rates of Explosion.

In attempting to calculate the rates of explosion from the formula there is some doubt as to what value should be adopted for the specific heat at constant volume. This constant has only been directly found at comparatively low temperatures. MM. Berthelot, Le Chatelier, and Mallard have made attempts to find the specific heats of the elementary gases and of cirbon monoxide at high temperatures by measuring the pressure of explosion. Berthelot arrives at the conclusion that the spesific heat at constant volume increases with the temperature, and at $4400^{\circ}$ C. attains the value $9 \cdot 6$. M. Berthelot's experiments do not, however, agree with those of MM. Le Chatelier and Mallard, and two series of experiments conducted by the latter experimenters do not agree with one another. The specific heat at constant volume may, however, be calculated from the velocity of explosion with the aid of the proposed formula. A few explosions have therefore been selected and the specific heats and temperatures calculated from them; specific heats at intermediate temperatures being found by interpolation. It was immediately perceived that the specific heats of $\mathrm{O}_{2}, \mathrm{H}_{2}$, $\mathrm{N}_{2}$, and CO might for all practical purposes be taken as identical at all temperatures.

A few words are necessary regarding explosions in which water is formed. If the specific heat of steam is taken as $\frac{3}{2} \times$ specific heat of the diatomic gases, the found rates of explosion fall below the calculated rates when the dilution with inert gas is great, and vice versa when the dilution is small. It is possible to account for this by two theories. The first theory is that at high temperatures the water is dissociated, whereas at low temperatures the combination of hydrogen and oxygen is complete. The second theory is that the specific heat H 2
Table I.
$x^{2}\left\{\begin{array}{l}\left.\frac{\mathrm{V}^{2} \mu}{2 \mathrm{RJ}}-(2 m-n) t_{0}\right\}-2 x\left\{h+t_{0}(3 m-2 n)\right\}-2\left\{h+2 t_{0}(m-n)\right\} . ~\end{array}\right.$

| Mixture. | Equation. | $x$. | App. temp. | Specific heat of $\mathrm{H}_{2} \mathrm{O}$. |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $2 \mathrm{H}_{2}+2 \mathrm{O}_{2}=2 \mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2}$ | 21,654 $x^{2}-234,572 x-232,856$ | 11.748 | $\begin{aligned} & { }^{\circ} \mathrm{C} . \\ & 3606 \end{aligned}$ | A. | $13 \cdot 80$ |  |
| $2 \mathrm{H}_{2}+4 \mathrm{O}_{2}=2 \mathrm{H}_{2} \mathrm{O}+3 \mathrm{O}_{2}$ | 28,417 $x^{2}-235,716 x-232,856$ | $9 \cdot 186$ | 2833 | B. | 11.64 |  |
| $2 \mathrm{H}_{2}+6 \mathrm{O}_{2}=2 \mathrm{H}_{2} \mathrm{O}+5 \mathrm{O}_{2}$ | 32,728 $x^{2}-236,860 x-232,856$ | 8.114 | 2340 | c. | $9 \cdot 67$ |  |
| $2 \mathrm{H}_{2}+\mathrm{O}_{2}+\mathrm{N}_{2}=2 \mathrm{H}_{2} \mathrm{O}+\mathrm{N}_{2}$ | 22,145 $x^{2}-234,572 x-232,856$ | 11:506 | 3675 | A. | $13 \cdot 11$ |  |
| $4 \mathrm{H}_{2}+\mathrm{O}_{2}=2 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{H}_{2}$ | 24,906 $x^{2}-235,144 \times-232,856$ | 10.345 | 3113 |  | $13 \cdot 44$ |  |
| $2 \mathrm{H}_{2}+\mathrm{O}_{2}+3 \mathrm{~N}_{2}=2 \mathrm{H}_{2} \mathrm{O}+3 \mathrm{~N}_{2}$ | 29,420 ${ }^{2}-235,716 x-232,856$ | 8.904 | 2914 | B. | 10,92 |  |
| $2 \mathrm{H}_{2}+\mathrm{O}_{2}+5 \mathrm{~N}_{2}=2 \mathrm{H}_{2} \mathrm{O}+5 \mathrm{~N}_{2}$ | 33,521 $x^{2}-236,860 x-232,856$ | $7 \cdot 941$ | 2391 | C. | $9 \cdot 05$ |  |
| $6 \mathrm{H}_{2}+\mathrm{O}_{2}=2 \mathrm{H}_{2} \mathrm{O}+4 \mathrm{H}_{2}$ | 31,581 $x^{2}-236,288 x-232,856$ | $8 \cdot 364$ | 2617 |  |  |  |
|  | 34,112 $x^{2}-237,432 x-232,856$ | $7 \cdot 832$ | 2153 | D. | 8.91 |  |
| Mixture. | Equation. | $x$. | App. temp. | $v$. | $\mu$. | H. |
| $\mathrm{C}_{2} \mathrm{~N}_{2}+\mathrm{O}_{2}=2 \mathrm{CO}+\mathrm{N}_{2}$ | 36,557 $x^{2}-254,860 x-253,144$ | 7.653 | ${ }^{\circ} \mathrm{C} .$ | 2728 | 84 |  |
| $\mathrm{C}_{2} \mathrm{~N}_{2}+3 \mathrm{O}_{2}=2 \mathrm{CO}+\mathrm{N}_{2}+2 \mathrm{O}_{2}$ | 38,023 $x^{2}-256,004 x-253,144$ | 7.608 | 3598 | 2110 | 148 | 126,000 |
| $\mathrm{C}, \mathrm{N}_{2}+2 \mathrm{~N}_{2} \mathrm{O}=2 \mathrm{OO}+3 \mathrm{~N}_{2}$ | 48,845 $x^{2}-327,432 x-325,288$ | 7.571 | 4552 | 2454 | 140 |  |
| $\mathrm{O}_{2} \mathrm{~N}_{2}+2 \mathrm{~N}_{2} \mathrm{O}+\mathrm{N}_{2}=2 \mathrm{OO}+4 \mathrm{~N}_{2}$ | 50,521 $x^{2}-328,720 x-325,288$ | $7 \cdot 379$ | 3933 | 2283 | 168 | 161,500 |
| $\mathrm{C}_{2} \mathrm{H}_{4}+\mathrm{O}_{2}=2 \mathrm{CO}+2 \mathrm{H}_{2}$ | 21,027 $x^{2}-139,776 x-137,488$ | $7 \cdot 517$ | 2534 | 2507 | 60 | 67,600 |
| $2 \mathrm{H}_{2}+\mathrm{O}_{2}=2 \mathrm{H}_{2} \mathrm{O} \ldots \ldots \ldots \ldots$. | 16,992 $x^{2}-234,000 x-232,856$ | 14.703 | 4265 | 2821 | 36 | 234,000 |
| $\mathrm{C}_{2} \mathrm{~N}_{2}+\mathrm{O}_{2}+2 \mathrm{~N}_{2}=2 \mathrm{CO}+3 \mathrm{~N}_{2}$. | 37,787 $x^{2}-256,004 x-255,144$ | 7.651 | 3841 | 2163 | 140 | 126,000 |
| $\mathrm{C}_{2} \mathrm{~N}_{2}+2 \mathrm{~N}_{2} \mathrm{O}+2 \mathrm{~N}_{2}=2 \mathrm{CO}+5 \mathrm{~N}_{2} \ldots \ldots \ldots \ldots \ldots \ldots$ | 49,456 $x^{2}-329,292 x-325,288$ | $7 \cdot 531$ | 3349 | 2098 | 196 | 161,500 |

of steam rises more rapidly with the temperature than the specific heat of the diatomic gas. The theory of dissociation is rendered improbable by the fact that dilution of electrolytic gas with oxygen lowers the rates a little more than dilution with an equal volume of nitrogen. The adoption of such an hypothesis would render it necessary for us to suppose that the chemical reaction does not proceed to its limit. Moreover, it would make it difficult to calculate the rates whenever steam is formed, for it would then be impossible, with our present knowledge, to say how far the chemical reaction would proceed in any particular case. We are therefore encouraged to test the first theory, i. e. that the specific heat of steam rises more rapidly with the temperature than that of the diatomic gases. The specific heat of steam at different temperatures has therefore been calculated from a few selected rates, as in the case of the elementary gases; and the values thus found are used to calculate the other rates. The results are given below. (Table II.)

Table II.--Specific Heats at Different Temperatures. $w=$ specific heat of water. $g=$ specific heat of diatomic gases.

| $t$. | 5600. | 5000. | 5400. | 5300. | 5200. | 5100. | 5000. | 4900. | 4800. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  |  |  |
|  | 7.850 | 7839 | 7.828 | $7 \cdot 817$ | 7806 | 7795 | 7784 | 7.773 | 7.762 |
| $t$. | 4700. | 4600. | 4500. | 4400. | 4300. | 4200. | 4100. | 4000 | 3900. |
| $w$. |  |  |  |  | 14750 | 14.625 | $14 \cdot 467$ | $14 \cdot 297$ | 14.125 |
| $g$. | 7.751 | 7740 | 77.729 | 7718 | 7707 | 7696 | 7.685 | T. 674 | $7 \cdot 663$ |
| $t$. | 3800. | 3700. | 3600. | 3500. | 3400. | 3300. | 3200. | 3100. | 3000. |
| $w$. | 13.938 | 13750 | 13:547 | $13: 344$ | $13 \cdot 102$ | 12850 | 12:560 | 12250 | 11.891 |
| $g$.. | 7652 | $7 \cdot 641$ | $7 \cdot 630$ | 7.619 | 7608 | 7.597 | 7.586 | $7 \cdot 575$ | 7564 |
| $t$. | 2900. | 2800. | 2700. | 2600. | 2500. | 2400. | 2300. | 2200. | 2100. |
|  | 11.503 | 11.040 | 10.578 | 10.172 | 9797 | $9 \cdot 484$ | $9 \cdot 203$ | 9.000 | 8.828 |
| $g$. | $7 \cdot 553$ | 7.542 | 7.531 | 7.520 | 7.509 | 7498 | $7 \cdot 487$ | $7 \cdot 476$ | $7 \cdot 465$ |


| Table III. <br> Velocity of Explosion calculated from the Formula $\mathrm{V}^{2}=\frac{2 \mathrm{RJ}}{\mu \mathrm{C}_{v}^{2}}\left[\left\{(m-n) \mathrm{C}_{p}+m \mathrm{C}_{v}\right\} \mathrm{C}_{p} t_{0}+\left(\mathrm{C}_{p}+\mathrm{C}_{v}\right) h\right] .$ <br> A is the rst term in the expression for $\mathrm{V}^{2}$. Ch is the second term. |  |  |  |  |  |  |  |  | $\stackrel{\sim}{0}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Mixture. | $\mu$. | Ch . | A. | V. | Found. | $t$. | $\begin{aligned} & \text { Mean } \\ & \mathbf{C}_{v} . \end{aligned}$ | Remarks. |  |
|  | 102 | 2,731,000 | 203,610 | 2746 | 2732 | $\begin{gathered} { }^{\circ} \mathrm{O} . \\ 2418 \end{gathered}$ | 7.954 | Heat of combustion $=152,500$. | K |
| $6 \mathrm{H}_{2}+2 \mathrm{~N}_{2} \mathrm{O}=2 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{~N}_{2}+4 \mathrm{H}_{2}$ | 100 | 2,804,475 | 191,160 | 2720 | 2705 | 2612 | 8.195 |  | 9 |
| $4 \mathrm{H}_{2}+2 \mathrm{~N}_{2} \mathrm{O}=2 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{~N}_{2}+2 \mathrm{H}_{2} .$ | 96 | 3,082,940 | 173,676 | 2604 | 2545 | 3077 | $9 \cdot 108$ |  | $\checkmark$ |
| $2 \mathrm{H}_{2}+2 \mathrm{~N}_{2} \mathrm{O}=2 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{~N}_{2} \ldots \ldots$. | 92 | 3,602,050 | 158,409 | 2408 | 2305 | 3813 | 10.810 |  |  |
| $2 \mathrm{H}_{2}+2 \mathrm{~N}_{2} \mathrm{O}+2 \mathrm{~N}_{2}=2 \mathrm{H}_{2} \mathrm{O}+4 \mathrm{~N}_{2}$ | 148 | 3,082,910 | 173,676 | 2097 | 1991 | 3077 | $9 \cdot 108$ |  | $\stackrel{7}{8}$ |
| $2 \mathrm{H}_{2}+2 \mathrm{~N}_{2} \mathrm{O}+3 \mathrm{~N}_{2}=2 \mathrm{H}_{2} \mathrm{O}+5 \mathrm{~N}_{2}$ | 176 | 2,920,700 | 181,520 | 1993 | 1880 | 2826 | $8 \cdot 576$ |  |  |
| $4 \mathrm{NH}_{3}+3 \mathrm{O}_{2}=2 \mathrm{~N}_{2}+6 \mathrm{H}_{2} \mathrm{O} \ldots \ldots \ldots \ldots \ldots \ldots \ldots$. | 164 | 7,814,500 | 432,090 | 2431 | 2390 | 3480 | 11.876 | Heat of combustion $=303,452$. | 兑 |
| $2 \mathrm{NH}_{3}+3 \mathrm{~N}_{2} \mathrm{O}=4 \mathrm{~N}_{2}+3 \mathrm{H}_{2} \mathrm{O} \ldots \ldots \ldots \ldots \ldots \ldots$. | 166 | 4,431,400 | 311,730 | 2219 | 2200 | 3272 | 9.810 | $" \quad=204,976$. | $\bigcirc$ |
| $2 \mathrm{H}_{2}+2 \mathrm{O}_{2}=2 \mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots$. | 68 | 2,955,420 | 82,855 | 2340 | 2328 | 3640 | 11.63 | " $\quad$, 117,000 . | $\stackrel{5}{5}$ |
| $2 \mathrm{H}_{2}+4 \mathrm{O}_{2}=2 \mathrm{H}_{2} \mathrm{O}+3 \mathrm{O}_{2} \ldots \ldots \ldots \ldots \ldots \ldots \ldots$. | 132 | 2,355,912 | 107,677 | 1940 | 1927 | 2866 | $9 \cdot 068$ |  | \% |
| $2 \mathrm{H}_{2}+6 \mathrm{O}_{2}=2 \mathrm{H}_{2} \mathrm{O}+5 \mathrm{O}_{2}$ | 196 | 2,112,318 | 132,017 | 1720 | 1770 | 2365 | 8.027 |  |  |
| $2 \mathrm{H}_{2}+\mathrm{O}_{2}+\mathrm{N}_{2}=2 \mathrm{H}_{2} \mathrm{O}+\mathrm{N}_{2}$ | 64 | 2,955,420 | 82,855 | 2412 | 2426 | 3640 | 11.63 |  |  |
| $2 \mathrm{H}_{2}+\mathrm{O}_{2}+3 \mathrm{~N}_{2}=2 \mathrm{H}_{2} \mathrm{O}+3 \mathrm{~N}_{2}$ | 120 | 2,355,912 | 107,677 | 2035 | 2055 | 2866 | 9.068 |  |  |
| $2 \mathrm{H}_{2}+\mathrm{O}_{2}+5 \mathrm{~N}_{2}=2 \mathrm{H}_{2} \mathrm{O}+5 \mathrm{~N}_{2} \quad \ldots \ldots \ldots \ldots \ldots$. | 176 | 2,112,318 | 132,017 | 1811 | 1822 | 2365 | 8.027 |  |  |
| $4 \mathrm{H}_{2}+\mathrm{O}_{2}=2 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{H}_{2} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots$. | 40 | 2,588,040 | 97,240 | 3316 | 3268 | 3193 | $10 \cdot 06$ |  |  |
| $6 \mathrm{H}_{2}+\mathrm{O}_{2}=2 \mathrm{H}_{2} \mathrm{O}+4 \mathrm{H}_{2} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots$. | 44 | 2,201,706 | 119,262 | 3517 | 3527 | 2605 | $8 \cdot 409$ |  |  |
| $8 \mathrm{H}_{2}+\mathrm{O}_{2}=2 \mathrm{H}_{2} \mathrm{O}+6 \mathrm{H}_{2} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots$ | 48 | 2,066,688 | 148,434 | 3532 | 3532 | 2153 | $7 \cdot 832$ |  |  |



On referring to the explosion of ethylene with excess of oxygen it is seen that $\mathrm{CO}_{2}$ is not completely dissociated until a temperature of $3500^{\circ} \mathrm{C}$. is reached. In all cases the temperature of explosion of cyanogen with excess of oxygen is above this, and therefore $\mathrm{CO}_{2}$ is never formed.

## The Pressure of Explosion.

The maximum pressure of explosion may be calculated with the aid of the two formulæ
and

$$
\left.\begin{array}{r}
p-p_{0}=\frac{\mu \mathrm{V}^{2}}{v_{0}^{2}}\left(v_{0}-v\right), \\
v=\frac{\mathrm{C}_{p}}{\mathrm{C}_{p}+\mathrm{C}_{v}} v_{0}
\end{array}\right\}
$$

These two equations lead to the formula

$$
p=\frac{\mu \mathrm{V}^{2}}{v_{0}} \frac{\mathrm{C}_{v}}{\mathrm{C}_{p}+\mathrm{C}_{v}}+p_{0} .
$$

The pressure for an explosion of equal volumes of cyanogen and oxygen calculated from this formula is 57 atmospheres. Jones and Bower* by breaking glass tubes obtain the value 58 atmospheres
VII. The Aqueous Fusion of Glass, its Relation to Pressure and Temperature. First Paper. By Carl Barus $\dagger$.
SOME time ago I published $\ddagger$ a series of results due to the action of hot water at $185^{\circ}$ on glass, the water being kept liquid by pressure. It was shown that the water contained in sealed capillary glass tubes increased in compressibility while it steadily diminished in bulk, as described in the subjoined summary of two consistent experiments with different tubes. During the observations the column soon became turbid, but it remained translucent enough to admit of measurement. As the action at $185^{\circ}$ proceeded, the length of the thread of water decreased. This thread was contained within the walls of the tube between two terminal threads of mercury (the lower being movable and transmitting pressure), and therefore decrease in the length of the thread can only mean contraction of volume of the system of glass and water in contact. The results are as follows:$\tilde{\theta}$ denoting the temperature of the capillary thread (maintained constant by a transparent vapour-bath) ; $t$ the time

* Journal of the Manchester Lit. and Phil. Soc. 1898.
$\dagger$ Communicated by the Author.
$\ddagger$ Barus: American Jouraal of Science, xli. p. 110 (1891).


[^0]:    * Communicated by Prof. Dixon, F.R.S.

[^1]:    * In the earlier researches Berthelot's theory was accepted as a working hypothesis. It was only after the difficulties attending the measurement of the rates of explosion in mixtures containing inert gases had been overcome that the inadequacy of Berthelot's theory became evident and the superiority of the sound-wave theory could be demonstrated.

