increase the extent to which the salt distils over the vessel surface, altering the structure and also presumably the chain-breaking efficiency. From the experimental point of view, therefore, the value of $E_0$ as determined in a potassium chloride-coated vessel must be regarded as the more reliable.

In conclusion, however, it may be said that the results give general support to the conclusion already reached from the dependence of the function $f_1$ on the concentrations of the reacting gases, namely, that the gas phase dissociation of hydrogen molecules is the principal method of chain initiation under the conditions employed.

**Reference**


---

The mechanism of the hydrogen-oxygen reaction

V. The reaction in vessels coated with alkali iodides

**BY C. F. CULLIS AND C. N. HINSHELWOOD, F.R.S.**

(Received 28 August 1945)

Previous work on the hydrogen-oxygen combination in vessels coated with alkali halides showed that with the iodides the temperature dependence of the reaction rate is abnormal. In iodide-coated vessels the whole mechanism of the reaction is now shown to be different: the greatly reduced rate is independent of $[H_2]$, proportional to $a + b[O_2]$ and independent of added nitrogen, all in sharp contrast with what is found in chloride-coated vessels. The normal reaction is thought to be completely suppressed by minute amounts of iodine liberated into the gas phase, a residual surface reaction being measured. The chemical actions which must be assumed to occur between the iodide and the gases provide indirect evidence for the probable mode of operation of the other halide salts in controlling the hydrogen-oxygen combination.

**Introduction**

In Part III (Willbourn & Hinshelwood 1945) it was shown that the temperature dependence of the hydrogen-oxygen reaction between the second and third explosion limits is much smaller in vessels coated with potassium or caesium iodide than in similar vessels coated with the chlorides. It has now been shown that in iodide-coated vessels the whole nature of the reaction is radically altered. From the investigation of this abnormal reaction inferences may be drawn about the probable mode of action of the alkali halides in general.
Experimental results

The experimental results may be stated as follows:

(1) The second explosion limit. At lower temperatures the value of the limit is almost the same as that found in a chloride-coated vessel, but, as the temperature is raised, the results become increasingly erratic. They are markedly dependent upon the rate of withdrawal of the gases from the reaction vessel, the limit becoming lower as this rate is decreased. At high temperatures the lowering of the limit becomes very considerable, until finally the low-pressure explosion region is completely wiped out.

(2) The rate of reaction between the second and third limits. (a) The rate is independent of hydrogen pressure even at the highest temperatures at which measurements can be made, as shown by some typical results in table 1.

Table 1. Dependence of rate on hydrogen pressure in potassium iodide-coated vessel at 570° C. Oxygen pressure 100 mm.

<table>
<thead>
<tr>
<th>$P_{H_2}$ (mm.)</th>
<th>250</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>450</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>rate (mm./min.)</td>
<td>6-4</td>
<td>6-6</td>
<td>6-7</td>
<td>6-5</td>
<td>6-6</td>
<td>6-9</td>
</tr>
</tbody>
</table>

(b) The rate increases nearly in proportion to the oxygen pressure, being represented by the expression $a + bP_{O_2}$, $a$ and $b$ being constants at a given temperature. An example is shown in table 2.

Table 2. Dependence of rate on oxygen pressure at 570° C. Hydrogen pressure 300 mm.

<table>
<thead>
<tr>
<th>$P_{O_2}$ (mm.)</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>rate (mm./min.)</td>
<td>6-6</td>
<td>9-6</td>
<td>11-6</td>
<td>13-0</td>
<td>16-7</td>
</tr>
</tbody>
</table>

(c) The rate is unaffected by additions of water vapour or of nitrogen (table 3).

Table 3. Influence of nitrogen on rate at 584° C. Oxygen 100 mm.: hydrogen 300 mm.

<table>
<thead>
<tr>
<th>$P_{N_2}$ (mm.)</th>
<th>0</th>
<th>50</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>rate (mm./min.)</td>
<td>13-2</td>
<td>13-4</td>
<td>14-0</td>
<td>13-0</td>
</tr>
</tbody>
</table>

(d) The pressure-time curves do not show the usual autocatalytic effects.

(3) The third explosion limit. The gases do not explode below 610° C, whereas in the same vessel coated with potassium chloride the explosion occurred at about 570° C for comparable pressures. At the high temperature in the iodide-coated bulb
The explosion seemed to be purely thermal: there was no induction period, and the rate just below the limit was very high. Added nitrogen did not lower the limiting pressures of the reacting gases.

Discussion of results

It is quite evident that the normal gas-phase reaction has been almost entirely replaced by a reaction of a quite different character. This is almost certainly due to the liberation of small quantities of iodine by the action of hydrogen on the salt and subsequent decomposition and oxidation of hydrogen iodide. Iodine acts as a very powerful inhibitor of the gas-phase reaction (Garstang & Hinshelwood 1931a,b). This view is supported by the observation that after an explosion the condensed water was coloured faintly brown. A very minute trace of iodine would be enough to explain the effects on the second limit and the suppression of the normal reaction. On the other hand, water could continue to be formed by the cyclical formation and oxidation of hydrogen iodide (as was shown in the earlier work on the action of added iodine).

A full and detailed theory of the processes occurring in the iodide-coated vessel would be extremely complex, involving, inter alia, the rate of diffusion of chain carriers or iodine to or from the surface, the reversible formation of hydrogen iodide from iodine, and the oxidation of the hydrogen iodide both on the surface and in the gas phase. An approximate interpretation can, however, be indicated. Nitrogen has little effect on the rate, therefore the overall influence of diffusion on the measured rate may be neglected for the purposes of an approximate treatment, and all reactions save surface reactions left out of account. The rate is independent of $[H_2]$ and nearly proportional to $[O_2]$. This would be most simply accounted for by assuming direct attack by oxygen on a surface whose constitution is independent of $[H_2]$. If the potassium iodide surface, by the action of hydrogen, became saturated with adsorbed hydrogen iodide, then the required condition would be fulfilled. The formation of potassium hydride and hydrogen iodide in the surface layer is quite probable, and the frequency of occurrence of the latter in the mosaic of atoms, ions and adsorbed molecules could be nearly independent of hydrogen. The oxidation of the hydrogen iodide would lead to the escape of iodine into the gas phase where its extraordinarily powerful inhibiting effect would be manifested.

Although it would be scarcely profitable to work out the full details of the mechanism, the general result is of interest in that it supports the view that all salts exert their effects essentially by their ability to enter into definite chemical reactions of the following type (cf. Part III):

$$KX + H = K + HX, \quad KX + H = KH + X,$$

$X$ being a halogen atom.

Caesium iodide would obviously be expected to behave like potassium iodide.

With chlorides, hydrogen chloride would be formed though to an extent which, in view of the considerations mentioned in Part III, would be difficult to predict.
It would be less susceptible to oxidation and decomposition, and even if appreciable amounts of chlorine escaped into the gas phase, their inhibiting effect would be very much less marked (as has been directly shown), since chlorine atoms continue the well-known Nernst chain. This means that chlorine is not an effective remover of hydrogen atoms. Thus we can have the inhibiting effect of the salt surface without the accompanying effects of powerful chain breakers in the gas phase.

REFERENCES


The drag of cylinders in fluids at slow speeds

BY C. M. WHITE, Imperial College, London

(Communicated by R. Bagnold, F.R.S.—Received 7 April 1945)

Experiments with wires falling sideways in viscous fluids are described. At very slow speeds the resistance is found to be independent of the density of the fluid when the fluid is finite in extent. In such purely viscous motion the boundary distance controls the pattern and Reynolds's number is without significance. At higher speeds the resistance becomes independent of this distance and agrees with Lamb's solution for a cylinder in an infinite fluid. At still higher speeds the experiments close the gap between the upper limit of validity of Lamb's approximations and the lower end of the wind-tunnel experimental range. The present experiments include Reynolds's numbers ranging from $10^{-5}$ to $10^{+2}$: at low speed the influence of distant boundaries is unexpectedly great, and Lamb's formula is much more restricted in scope than usually thought; when the Reynolds number is $10^{-4}$ the presence of boundaries 500 diameters away multiplies the drag two-fold.

Notation

\[
\begin{align*}
P &= \text{drag per unit length of cylinder } (MT^{-2}). \\
\tau &= P/d = \text{net weight of cylinder/dL } (ML^{-1}T^{-2}). \\
L &= \text{length of cylinder } (L). \\
d &= \text{diameter of cylinder } (L). \\
D &= \text{diameter of container } (L). \\
v &= \text{speed } (LT^{-1}). \\
\mu &= \text{viscosity of fluid } (ML^{-1}T^{-1}). \\
\rho &= \text{density of fluid } (ML^{-3}). \\
R_1 &= \text{Reynolds number, } \rho vd/\mu. \\
R_2 &= \text{Reynolds number, } \rho vD/\mu.
\end{align*}
\]