CLXXII.—*The Inhibition of the Glow of Phosphorus.*

By HARRY JULIUS EMELÉUS.

THE slow luminous oxidation of phosphorus is influenced by the addition of a gas or vapour in one of two ways. Gases such as hydrogen, nitrogen, and carbon dioxide effect a dilution, and the kinetics of the reaction continue to obey the law of mass action. In other cases, however, (*e.g.*, many organic vapours) a small concentration of the added substance stops the reaction and the accompanying phenomena of ionisation and formation of ozone. Phosphorus has, moreover, the remarkable property of oxidising much more slowly, and without luminescence, in pure oxygen when the partial pressure of this gas exceeds a limiting value determined by the temperature. The existence of such a pressure is readily demonstrated by gradually evacuating a vessel containing phosphorus and oxygen. At atmospheric pressure, the reaction is imperceptible, but when the "glow pressure" is reached the phosphorus surface lights up suddenly as the normal oxidation begins. Apparently in this case the oxidation is inhibited by oxygen itself.

Various suggestions have been made to account for these anomalies. One of the earliest was that the ozone formed during the reaction was an essential catalyst, and that it was destroyed by the poisons (Schönbein, *J. pr. Chem.*, 1845, **36**, 246). It is remarkable how often such a reaction is found to be possible. For example, turpentine, ethylene, and benzene can all act as inhibitors, and all react readily with ozone, yet in other cases any such action is very much feebler. Qualitative tests were made to examine the action of ozone on acetone, methyl ethyl ketone, hexane, chlorobenzene, and ethyl iodide. The first three gave definite evidence of a slow reaction, whilst the last two were more readily attacked. It is evidently wrong to assert that any of these substances is quite inert. If this were the true explanation of inhibition, however, the relative activity of different poisons would presumably be that of their reactivity towards ozone, and in some cases this is not so; *e.g.*, acetone is a stronger poison than benzene, but is less readily attacked by ozone.

The alternative suggestion that poisons form protective surface films on the solid phosphorus is unlikely, for Centnerszwer has shown that phosphorus exerts its normal vapour pressure in presence of inhibitors (*Z. physikal. Chem.*, 1913, **85**, 99).

The view now generally held is that the propagation of the glow is a process analogous to the passage of a flame through a combustible gas mixture, and that poisons prevent this from occurring. Lord Rayleigh has, in fact, shown that this is probably correct in the particular case of inhibition by excess of oxygen (*Proc. Roy. Soc.*, 1923, *A*, **104**, 322). Extending the earlier experiments of Bloch (*Compt. rend.*, 1908, **147**, 842), he measured the blast of gas necessary to blow the glow from a given phosphorus surface in various oxygen–nitrogen mixtures, and found that it became less as the percentage of oxygen was increased. Assuming that the blast required to maintain the glow in a stationary position downstream is a measure of the virtual rate of propagation upstream, it follows that successive increases in the oxygen concentration decrease the rate of propagation.

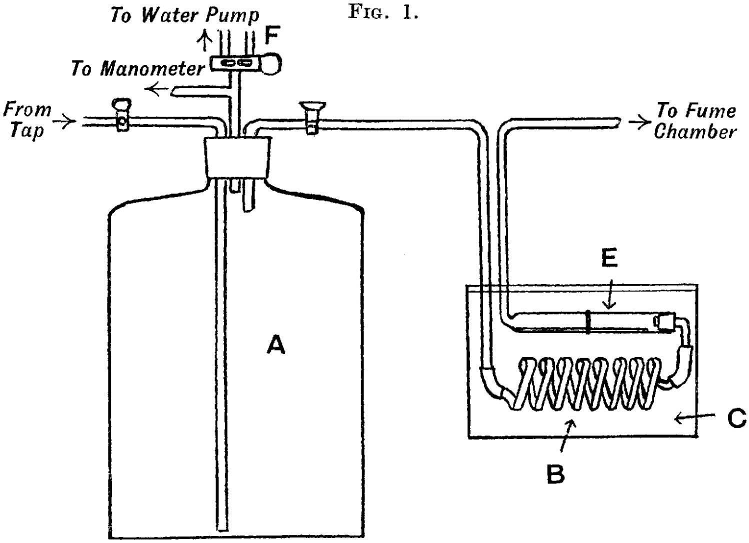
The position of oxygen is unique, since it both supports and inhibits combustion, and it cannot be assumed *a priori* that the more active poisons act in the same way. In the experiments to be described, this point has been studied by applying Lord Rayleigh's method of investigation to the propagation of the glow in presence of the strong inhibitors ethylene, benzene, chloroform, and aniline, and results similar to those for oxygen have been obtained.

The Propagation of the Glow of Phosphorus in the Presence of Inhibiting Substances.

The phosphorus used throughout was purified by an acid dichromate solution, as described by Downey (J., 1924, **125**, 347). Oxygen was obtained from a cylinder.

The apparatus consisted of a large bottle, A (Fig. 1), into which water was run from the tap. The gas stream so produced was passed through the metal coil, B, where it attained the temperature of the bath, C, and then over a flat phosphorus surface cast in the cylindrical tube, E (14 cm. long, 1 cm. internal diameter). Round E, about half-way along, a narrow black band was fixed, and in all the experiments the gas stream was adjusted so as to blow the glow from the phosphorus surface up to this mark. From a direct measurement of the rate at which water was flowing into A, the velocity of the blast through E could be calculated.

FIG. 1.

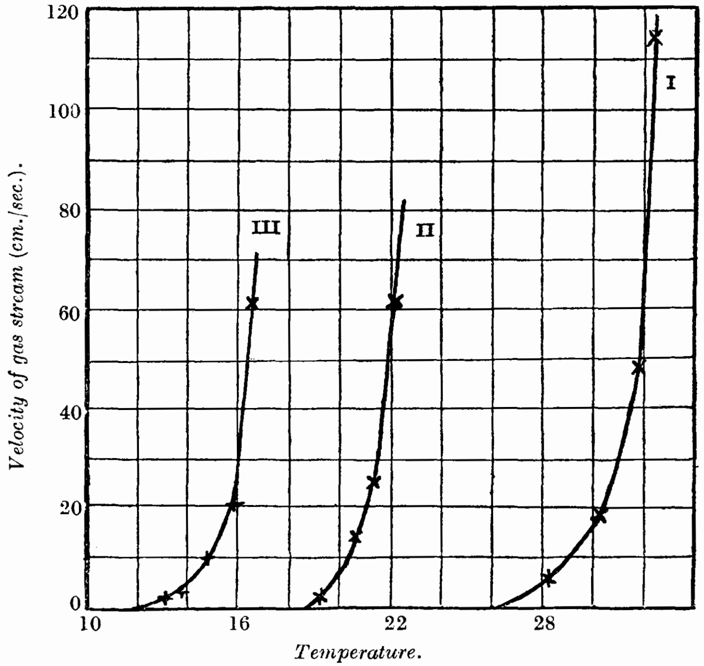


Dependence of the Blast upon the Percentage of Ethylene added to the Air.—To obtain the low concentrations of ethylene (less than 0·5%), a mixture of ethylene and air in known proportions was prepared in a gas holder connected to F (Fig. 1). A was then evacuated, and the ethylene–air mixture and air were admitted in the desired proportions as indicated by the mercury manometer. The solubility of the ethylene in the water during the short time of contact was neglected as being within the limits of experimental error. The same phosphorus surface was used throughout. Measurements of the gas stream needed to blow the glow to the mark were made for different ethylene concentrations at a temperature of 20°. In this way, a series of relative values was obtained, showing the influence of the admixed gas on the propagation of the glow :

Velocity of gas stream (cm./sec.)	140	31	24	17	8	1	1
% Ethylene (by volume)	0·16	0·26	0·28	0·36	0·38	0·43	0·46

With less than 0·15% of ethylene the greatest gas stream obtainable was insufficient to blow the glow off the phosphorus surface. As the ethylene concentration was increased it became easier to blow the glow away, and complete inhibition occurred at a concentration of 0·45%.

FIG. 2.



Air saturated (I) *with benzene ;* (II) *with chloroform ;* (III) *with aniline.*

Dependence of the Blast upon the Temperature, in the Presence of a Constant Concentration of Inhibiting Substance.—Three typical poisons, benzene, chloroform, and aniline, were introduced in large excess into A (Fig. 1) in successive series of experiments, and the air was allowed to become saturated with the vapour at room temperature (16°). The blast of saturated gas which just sufficed to clear the phosphorus surface of luminosity was then determined as already described for various temperatures of the bath, C. The results are reproduced in Fig. 2. In each case the glow was inhibited below a certain temperature, and above this it became increasingly difficult to blow it away.

If Lord Rayleigh's assumption be adopted, it follows from these results that the typical poisons studied act by reducing the rate of propagation of the glow in the gas mixture. Complete inhibition of the luminous oxidation marks the limit of this effect with increasing concentration of inhibitor. It is very probable, therefore, that oxygen acts in the same way as the more active poisons. A discussion of the possible mechanism of inhibition is given later. These considerations might seem inapplicable to the conditions under which the glow of phosphorus is generally seen, *viz.*, as a surface luminosity. The establishment of this intense surface oxidation is, however, often preceded by the passage of a luminous pulse through the gas mixture, resulting in the production of ozone, which tends to localise the reaction.

The Influence of Temperature on the Action of Inhibiting Substances.

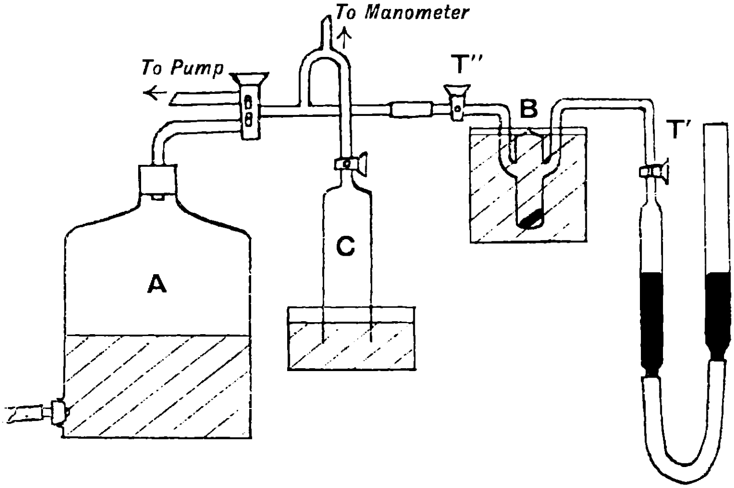
The effect of " poisons " depends both on the pressure and on the temperature. The influence of pressure was investigated by Centnerszwer (*Z. physikal. Chem.*, 1898, **26**, 1). Phosphorus was introduced into a mixture of oxygen with the inhibiting vapour, and the pressure was reduced until the glow appeared. In every case the limit was lower the greater the concentration of the inhibitor. The present experiments represent an attempt to make a similar systematic study of the influence of temperature. Ethylene has been used, since it is not only a strong poison, but is inert towards phosphorus. Probably it is typical, however, for experiments made with carbon disulphide and ethyl iodide gave similar although less consistent results.

The apparatus used is shown in Fig. 3. Ethylene was prepared from phosphoric acid and absolute alcohol, washed by water and sulphuric acid, and collected over water in A. Between 2—5 g. of purified phosphorus were sealed up in the tube B of 30 c.c. capacity, which was immersed in a freezing mixture and evacuated, with the tap T′ closed and the space below it filled with mercury. B was then put in melting ice, and ethylene was admitted from A. After allowing time for diffusion, moist air or oxygen was passed in from C until the total pressure was that of the atmosphere. The tap T″ was then closed and T′ opened. B was heated gradually on a water-bath over a resistance mat, and the temperature at which the glow appeared was recorded. During heating, the pressure in the apparatus was kept constant by adjusting the levelling tube,

L. Between successive experiments with different ethylene–air mixtures, the space below T′ was filled with mercury, T′ was closed, B was cooled, and the apparatus was alternately evacuated and filled with air a number of times. Some consecutive pairs of observations were made with the same phosphorus, in which a definite partial pressure of ethylene was established first in air and then in oxygen. Such readings were strictly comparable, and differed by less than 3°. The oxygen–ethylene mixtures frequently detonated shortly after the phosphorus had begun to glow.

Experiments were made at constant volume by raising the tube L (Fig. 3). The resulting increase in pressure amounted at the highest temperature employed to approximately half an atmosphere, and a corresponding increase in the glow temperature of 5—10° was recorded. The results are shown graphically in Fig. 4.

FIG. 3.

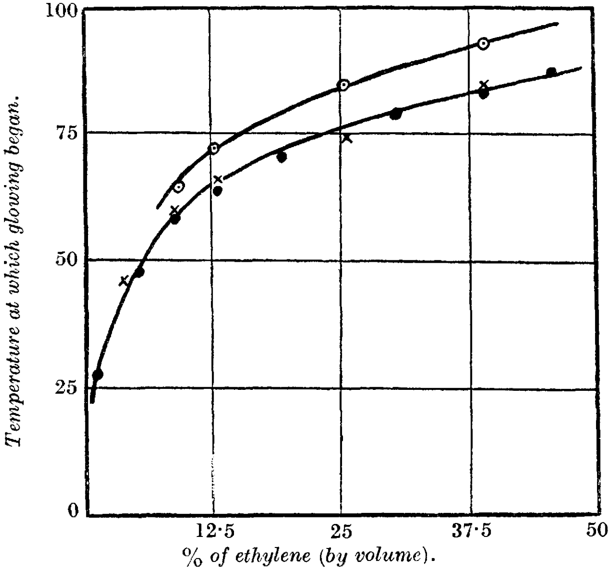


The main source of error in these experiments was in the observation of the glow. Even with thoroughly rested eyes it was difficult to determine in some cases whether a glow was occurring or not, especially with the high ethylene concentrations.

Two points of special interest are brought out by these results. The temperature at which the glow first occurred appeared to be determined by the concentration of the ethylene, irrespective of whether it was mixed with air or oxygen ; also the luminous oxidation was inhibited at temperatures well above the normal ignition-point of phosphorus, which is about 60°.

Although these experiments leave little doubt as to the absence of luminous oxidation below a definite temperature, a number of tests were made to determine if any non-luminous oxidation occurred. Purified phosphorus (1—2 g.) was sealed in tubes of 40 c.c. capacity (1·5 cm. diameter), having a quill tube fused to one end and drawn down to a capillary about 20 cm. from the wider tube. The whole tube up to the capillary was cooled in a freezing mixture and evacuated ; the freezing mixture was replaced by melting ice, moist ethylene and air were admitted in the desired proportions, as indicated by the pressure, and the tube was sealed at the capillary. Two series of bulbs, containing 8% and 26%, respectively, of ethylene were heated in the dark in a thermostat at 48° for 2 months, when they were opened by breaking the capillary under mercury, the bulb being inverted and cooled in ice. Any oxidation would be indicated by a rise of mercury in the stem, correction being made for change in barometric height. The bulbs containing 8% of ethylene exhibited a decrease in pressure of 2—12 cm. of mercury, whilst for those with 26% the decrease varied between 2—6 cm. Control tubes containing no phosphorus were unaltered. Further experiments are being made to verify that this slow rate of oxidation is maintained.

FIG. 4.



⊙ *Ethylene–air mixtures at constant volume.* × *Ethylene–oxygen mixtures at constant pressure.* ● *Ethylene–air mixtures at constant pressure.*

These results show that absorption of oxygen occurs when the luminous oxidation is inhibited, which is analogous to Lord Rayleigh's observation of a slow non-luminous oxidation in moist oxygen at atmospheric pressure (*Proc. Roy. Soc.*, 1924, *A*, **106**, 1).

Discussion.

Any account of the mechanism of inhibition must explain why either an increase in temperature or a decrease in pressure tends to produce the glow. The former involves at least two factors, since both the vapour pressure of the phosphorus and the potential rate of reaction increase. The experiments described have shown that inhibition can extend to 90°, which is much above the normal ignition temperature of phosphorus. Moreover, the "glow temperature" does not depend on whether air or oxygen is used as a diluent for the ethylene. When the glow is prevented, the tendency for the reaction to occur is demonstrated by the slow non-luminous oxidation which was observed at 48°. At some stage, depending on the ethylene concentration, the impediment is overcome and a wave of luminosity passes through the mixture, the subsequent oxidation being accelerated by the formation of ozone. Again, on slowly decreasing the pressure in a mixture of ethylene and oxygen, the partial pressure of the phosphorus will remain constant in the presence of the solid. In effect, therefore, the proportion of combustible vapour in the mixture is being increased, which in itself would be expected to favour flame propagation.

Several analogous cases have been recorded. White found that the vapours of benzene, acetaldehyde, acetone, and ether had "a powerful inhibitory effect on the propagation of flame in carbon disulphide–air mixtures" (J., 1922, **121**, 2561). The addition of 0·025% of ether, for example, necessitated the use of 25% more carbon disulphide if the mixture was to propagate flame. In Dixon's experiments on the phosphorescent flame of carbon disulphide, a very much higher temperature was required to produce ignition when a small amount of ethylene was added (*Rec. trav. chim.*, 1925, **44**, 305). Further examples are furnished by the many organic sulphur compounds studied by Delépine (*Bull. Soc. chim.*, 1922, **31**, 762). These contain the group C=S, or P=S, and undergo a luminous oxidation at room temperatures, which is inhibited by ether, acetone, and pyridine. Here also a decrease of pressure or an increase of temperature will restart the luminescent reaction after it has been arrested.

The experiments described have shown that the addition to air of typical inhibitors renders it easier to blow the glow from a phosphorus surface, and that increase in temperature diminishes this action. An analogy is thus established between the action of excess of oxygen and that of stronger poisons, in that both prevent the propagation of the glow in the gas. A tentative explanation of the mechanism was put forward by Lord Rayleigh, who suggested that in the propagation of the glow the products of the reaction in one layer acted as catalysts in the next. These catalytic particles are supposed to be rendered inactive by the adsorption of the inhibiting molecules, when the reaction stops. A similar view has been adopted by Dixon to explain the inhibition of the phosphorescent flame of carbon disulphide.

The author wishes to thank Professor H. B. Baker, F.R.S., for his kind interest and advice throughout this research. He is indebted to the Department of Scientific and Industrial Research for a maintenance grant, and to the Trustees of the Dixon Fund for a grant for the purchase of apparatus.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7.
[*Received, February 12th, 1926.*]