

## The Glow of Phosphorus.<sup>1</sup>

By the Right Hon. LORD RAYLEIGH, F.R.S.

THE discovery of phosphorus was one of those which is associated with the transitional period when magic and science flourished to some extent side by side, and when the borderline between them was not very well defined. The discovery seems to have been made by the alchemist Brand, of Hamburg. But in those days scientific discoveries were often cherished as valuable secrets, not so much for their commercial value as for the sense of superior knowledge and power which their exclusive possession was supposed to give. Scientific secrets are sometimes jealously guarded now, but not for this reason. When reticence is observed, it is for the less romantic motive of commercial advantage. In the absence of this motive, the scientific men of to-day tell all they know, and tell it without delay.

The subject of phosphorus emerged into daylight in 1678, when Kunkel, who had learnt the secret by word of mouth, made it public. In 1780 the Hon. Robert Boyle deposited a paper on the same subject with the Royal Society. He had worked it out anew, without more than the hint that phosphorus came from an animal source.

It was a long time before the nature of the luminosity of phosphorus was finally settled. The early investigators not unnaturally classed it with the substances which become luminous by exposure to light, such as impure calcium sulphide. This notion survives in the word "phosphorescence," which is after all purely descriptive of the property of giving light. Now, however, the word is usually reserved for the cases like calcium sulphide. Phosphorus is not commonly spoken of as phosphorescent; its luminosity, as every one now knows, is due to slow combustion in the oxygen of the air. It took a long time to prove this, and the question was still in a measure open down to the year 1874. The doubt arose partly from the extremely small quantity of oxygen necessary to make the phosphorus visibly luminous. Accidental leakages may thus confuse the question. Another puzzling circumstance was that when oxygen was substituted for air the glow was extinguished. This can be shown by means of a large flask containing phosphorus dissolved in olive oil. Though the flask may be full of oxygen, the phosphorus is quite dark. When, however, some of the oxygen is removed by means of an air-pump, the phosphorus suddenly blazes out at a lowered oxygen pressure. The same result may be shown by substituting air for oxygen.

This is not the only peculiar thing about the behaviour of glowing phosphorus. When a piece of cotton wool moistened with bisulphide of carbon is held above a dish containing an oily solution of phosphorus, so that the vapour can stream down from it on to the glowing surface, the vapour has an almost magical effect. It stops the phosphorus glowing altogether. In a little time, the small quantity of vapour gets dissipated, and the phosphorus glows again.

Bisulphide of carbon is only one example of many vapours which will behave in this way. Ammonia, camphor, ethylene, turpentine, and essential oils generally, will do the same thing, though they vary widely

as to their effectiveness. The majority of permanent gases have little effect in this way, though I am not prepared to say what they might do at high pressure.

It will probably be admitted on consideration that the action of oxygen is not essentially different from that of the other inhibiting substances. As will be explained shortly, the action occurs between oxygen and phosphorus vapour. A little oxygen is necessary to unite with the vapour as it comes away from the phosphorus surface, but the density that is of any use in this way is very small. If, for example, we have a millimetre of oxygen pressure, there will be in the gas space many oxygen molecules for one phosphorus molecule, and a further increase can scarcely promote the combustion. The action of a great excess of oxygen, as when we admit it up to atmospheric pressure, must be something quite different. There is therefore no real paradox in the quenching by an excess of oxygen. Perhaps this analogy may help to explain the action: A man cannot live without water; if he does not get it he will die of thirst; yet if he swallows too much he may be drowned. The water acts in quite different ways in the two cases, and so does oxygen in contact with phosphorus.

Another very strange thing happens when phosphorus is used to get rid of the last traces of oxygen in gas analysis. Suppose that we start with air in a confined space, and put a piece of phosphorus into it. At first the light is confined to the surface, but as the oxygen approaches exhaustion, the light is seen to become diffused throughout the volume of the vessel. It is easy to understand why this happens. Phosphorus is appreciably volatile at the ordinary temperature. When the surrounding oxygen is abundant it snaps up the phosphorus vapour at once, before it can diffuse away from the surface. But when oxygen becomes scarce the phosphorus has the chance to get some distance before this happens. This much is easy to understand. But if we look closely we see that the glow is not steady, but shows moving clouds of luminosity, most curious to watch. Any one can readily try this experiment. Nothing more is required than a piece of phosphorus stuck on a wire and introduced into a bottle standing inverted with its neck under water.

My own work on the subject started from this experiment, which I tried to develop into something more definite than clouds of vague outline moving in an ill-defined path. Fig. 1 shows an attempt in this

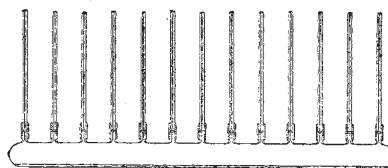


FIG. 1.

direction which had some success. The idea was to constrain the luminosity to move in one direction only. The horizontal tube has a layer of phosphorus lying along the bottom. The long narrow vertical tubes allow air to leak in slowly. When the oxygen originally in the tube is nearly exhausted, luminous pulses are

<sup>1</sup> Discourse delivered at the Royal Institution on Friday, June 6.

seen to spring into existence at the side openings, to divide, and to travel along the tube. Usually this happens predominantly at one or two particular places. Pulses travelling along the tube in opposite directions kill one another when they meet.

This arrangement was set up in a dark room, and watched from time to time. After the lapse of a week or more a change was noticed. Although nothing had

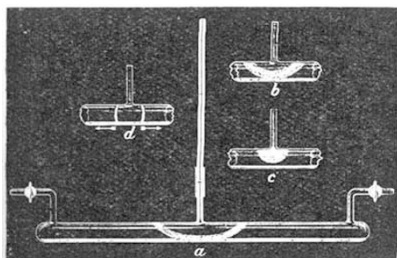


FIG. 2.

been touched, the movements were less lively, and the light had become stationary in places. Finally, all movement ceased.

What could be the explanation of this? The phosphorus had originally been melted into the tube under water, for safety, and the water was, so far as possible, poured off. But, of course, it could not be got rid of completely in that way. The oxides of phosphorus produced by the combustion are greedy of water, and thus had gradually dried the tube. On adding water the movements began again.

The next illustration (Fig. 2) shows a similar tube, with only one capillary entrance at the middle. It was dried out on the mercury pump in the first instance, and filled with nitrogen. A perfectly steady cloud of luminosity is seen when atmospheric oxygen begins to mingle with phosphorus vapour; *a*, *b* and *c* show successive stages as the oxygen influx is increased. If a drop or two of water is added a succession of luminous pulses starts at the side entrance, divides, and travels in opposite directions along the tube (Fig. 2, *d*).

Why does the luminosity move when there is water, and remain steady when there is none? It is evident that the travelling pulses represent the propagation of a wave of chemical action along the tube. There is a mixture of oxygen and phosphorus-vapour ready to unite. It does not at once do so, but chemical union is determined by the passage of the wave, just as in the firing of a train of gunpowder. Nothing of this kind seems, however, to happen in the absence of water. The water holds up the combustion.

Now that matters have been brought to this point, we may recall the experiment in which phosphorus was prevented from glowing by the presence of bisulphide of carbon vapour. Water, it is evident, acts like the other inhibiting substances, but less powerfully. This naturally suggests that we might get the travelling pulses on a more impressive scale by using a more powerful inhibitor than water. It is not desirable to have too powerful an inhibition, however, and I have found that camphor succeeds as well as anything. If a long horizontal glass tube with a mixture of camphor and phosphorus lying on the bottom is exhausted with an air pump, and air is allowed slowly to leak into it

through a fine adjustment valve at one end, bright luminous flashes pass down the tube at short intervals. The camphor vapour holds up the combustion until enough air has leaked in to make a mixture of favourable composition, the combustion starts, and the wave is propagated. The period evidently depends on how strong is the inhibiting action. Ammonia is a convenient inhibitor for illustrating this, for its action may be made as powerful as is desired by using a more concentrated solution. The period of the flashes is increased accordingly. The moving clouds of luminosity observed when the absorption of oxygen by phosphorus is nearly complete, are thus linked up quite naturally with the existence of inhibiting substances.

Another series of experiments bring out a further unification of the same kind. They began with the repetition of an interesting observation by L. and E. Bloch, which showed that if some phosphorus was placed in a glass tube, it was possible to blow the glow away from it by a blast of air, and maintain it at a distance downstream. In this form the experiment is rather difficult of control, sometimes succeeding and sometimes failing, for no very apparent reason; but I found it ultimately to be a matter of temperature, a few degrees making the whole difference. Fig. 3 shows the arrangements made by me to bring this under satisfactory control. The phosphorus is a thin flat strip, cast into a suitable recess in the side of a water tank; thus its temperature cannot differ much from that of the water. The latter can be varied at pleasure by the use of ice or warm water. A flat sheet of glass is held at a distance of a millimetre or two parallel to the phosphorus slab, and the air flows between the two, being confined by suitable packing strips at the sides. The channel is prolonged downstream of the phosphorus, and is made suddenly deeper about two inches down.

The accompanying photographs (Fig. 4) illustrate the effects obtained. No. I shows how the phosphorus surface looks without any blast. V shows the glow blown right off, and maintaining itself downstream, where the channel is deepened. The dotted line (inked in on the photograph) shows the position of the phosphorus slab, which is quite dark. This is essentially the Blochs' original experiment. Interesting as it

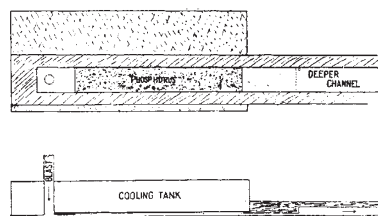


FIG. 3.

is, however, it by no means exhausts what we can learn with the arrangement described.

The effect of changes of temperature was examined, adjusting the blast in each case so that the glow was blown half-way down the phosphorus strip. The velocity of blast necessary to do this was found to diminish enormously as the temperature was reduced. Thus in cooling from room temperature to near the freezing-point, the velocity diminished a thousand times. I next tried altering the oxygen content, and

found to my astonishment that enriching the air with oxygen had the same effect as cooling, and diminished the necessary velocity of blast in an equally striking degree. In both these cases the ultimate result, when the velocity had been reduced to something of the order of 1 cm. per second, was to make the glow flickering and uncertain of maintenance. On cooling a little more, or adding a little more oxygen, it went out altogether.

Now we must remember a fact, often enough insisted upon nowadays, that motion is relative. We have thought so far of the blast acting on the stationary cloud of luminosity, but we might equally regard the cloud of luminosity as propagating itself in the reversed direction through still air. When the air is much enriched with oxygen the necessary blast is gentle—

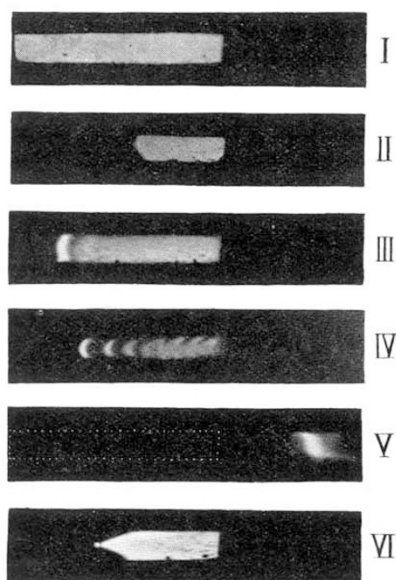


FIG. 4.

in other words, the propagation is slow. It appears then that *extinction is the limiting case of slow propagation*. If we can trace the cause of slow propagation the cause of extinction will not be far to seek.

Before passing to this, however, attention may be directed to some curious effects met with in the course of these experiments on the blast. The same sequence of changes occurs whether we reduce the temperature or increase the oxygen content. Suppose, for definiteness, that the latter course is followed. When the oxygen is very little, the glow tends to cling to particular spots, from which it cannot readily be detached. II shows this to some extent, though other experiments were made in which it was much more striking. On close examination it appeared that these special spots were depressions in the phosphorus surface, where there was partial shelter from the blast. At these places the glow started, and when once started, it infected the gas downstream of it, and made the blowing away impossible. VI shows this very clearly. In this case a hole was made intentionally.

As the oxygen content is increased a bright luminous head develops, followed by a darker space, and then uniform luminosity (III). This bright head no doubt

represents the combustion of the stock of phosphorus vapour accumulated as the blast passes over the dark surface.

The next stage, IV, is observed when the blast is so rich in oxygen that extinction is near. A succession of bright heads separated by dark spaces has now developed. This photograph was given four hours' exposure, and was not easily obtained: for some movement of the luminous heads is difficult to avoid during so long a time. The heads were seen quite regularly distributed along the column. The confusion on the right-hand side is due to unavoidable shifts.

The question arises as to why this propagation should occur at all, and why it should be slower when excess of oxygen is present. In the analogy of a train of gunpowder there is no doubt that propagation occurs primarily because each layer that has begun burning heats up the next layer, and causes it to burn too. In the case of phosphorus this explanation is scarcely tenable, because the phosphorus vapour present is only a very small fraction of the atmosphere in which it is contained, and it can be calculated that it cannot yield enough heat to raise the temperature more than a degree or two, which would not be enough.

We must look for some other way in which the action in one layer can help the action in the next; and the suggestion I make is that the action is of the kind called catalytic. It is true that this explanation is incomplete and in a measure speculative. On the other hand, it covers many facts otherwise very hard to co-ordinate. One of the most striking peculiarities of catalytic actions is the facility with which the catalyst is *poisoned*. The exact condition of a surface capable of producing this effect is a very critical thing, and I believe that when the glow of phosphorus is inhibited, it simply means that the particles of phosphoric oxide, or other product of combustion, are spoilt, or *poisoned* by the condensation of molecules of the inhibiting substances upon them; and that this prevents them from assisting the propagation. It is noteworthy that most of the inhibiting substances are easily condensable vapours, such as would be likely enough to act in this way. Oxygen is an exception, but it must be noticed, first, that oxygen will only act when moist; and, secondly, it has to be present in enormous excess—about 20,000 molecules of oxygen for one of phosphorus vapour—before it can quench the glow. Inhibitors like ammonia doubtless act by definite chemical union with phosphoric oxide.

Lastly, the view here explained requires us to suppose that the combination is always breaking out sporadically at isolated centres, though in the presence of an inhibitor it fails to propagate itself. I have recently been able to prove directly that this does in fact happen when oxygen is the inhibitor. When the gas-pressure was lowered the phosphorus glowed; but when it was raised again the phosphorus went out abruptly, like a candle blown out. Nevertheless, under the latter condition, it was found by observations lasting over several weeks, that a slow absorption was going on all the time, and that this action occurred between oxygen and the *vapour* of phosphorus.

This whole research has been rather off the main stream of scientific inquiry at the present time; but it shows that there is still a fascinating field for research about phenomena which have been familiar for centuries.