

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## THE OBLITERATION OF THE CHARACTERISTIC SPECTRA OF METALS BY CERTAIN GASES.

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In 1862 Mitscherlich<sup>1</sup> observed that the characteristic flame spectra of certain elements were entirely absent in the hydrogen-chlorine flame. Fredenhagen<sup>2</sup> noticed that the flames from which these spectra were emitted were all oxygen flames, and advanced the hypothesis that the ordinary flame spectra were due to the oxides of the elements, as an alternative to the hypothesis of Bunsen and Kirchoff<sup>3</sup> that the presence of the free metal in the flame was necessary for the production of the spectrum.

The theory of Stark<sup>4</sup> that the production of a spectrum line occurs only when an electron returns to a valence position, was apparently not in accord with the fact, observed by Fredenhagen, that the hydrogen-chlorine flame conducts electricity about as well as the oxygen-hydrogen flame. The experiments of Franck and Pringsheim<sup>5</sup> on the relative mobilities of the positive and negative carriers in the hydrogen-chlorine flame somewhat weakened this argument. They found that the positive carrier in the hydrogen-chlorine flame was much more mobile than the negative carrier, whereas in the hydrogen-oxygen flame conditions were reversed, the negative carrier exceeding in mobility the positive carrier by about four times. This is strong evidence in favor of the supposition that there are no free electrons in the hydrogen-chlorine flame, so that the conductivity of this flame would appear to be due largely to very mobile positive ions (possibly free hydrogen ions). At the end of their paper, Franck and Pringsheim mention that they were able to produce the D-lines of sodium in the interior of the hydrogen-chlorine flame by passing a spark through the flame between platinum electrodes coated with sodium chloride.

The absence of free electrons in the hydrogen-chlorine flame and their presence in the hydrogen-oxygen flame might be explained either as due to the non-production of electrons in the reaction between hydrogen and chlorine or by the complete removal of electrons, as soon as they are formed, by the excess of chlorine in the flame.

<sup>1</sup> Mitscherlich, *Pogg. Ann.*, **116**, 499 (1862).

<sup>2</sup> Fredenhagen, *Ann. Physik*, **20**, 133 (1906).

<sup>3</sup> Bunsen and Kirchoff, *Pogg. Ann.*, **113**, 337 (1861).

<sup>4</sup> Stark, *Ann. Physik*, **29**, 316 (1909).

<sup>5</sup> Franck and Pringsheim, *Verh. deut. physik Ges.*, **13**, 328 (1911)

### Experiments on Flame Spectra.

The method used by all previous observers to produce the hydrogen-chlorine flame was to obtain first a flame of hydrogen burning in oxygen and then to displace the oxygen by chlorine. In such a flame the electrons, if produced by the reaction taking place at the boundary between the two gases, would at once proceed to an atmosphere containing a large excess of chlorine, which might remove them before they had time to collide sufficiently with the sodium or other ions to produce an appreciable luminosity. It was thought, therefore, that the lines might be obtained in a flame of chlorine burning in hydrogen, where the incandescent gas produced at the boundary proceeds to a region nearly devoid of chlorine. This was found to be the case.

Hydrogen was led downwards through a tube about 25 mm. in diameter and escaped at the lower end, where it was allowed to burn in air. A jet of chlorine gas, issuing from a quartz nozzle, was then inserted upwards, through the flame of hydrogen burning in air, into the atmosphere of hydrogen above the flame. In this way the chlorine was ignited and continued to burn in the atmosphere of hydrogen. When the quartz nozzle was charged with sodium chloride, by dipping it into a solution of the salt, the yellow light of sodium could readily be observed in the outer portion of the flame, while the inner portion, rich in chlorine, was devoid of all trace of sodium light. It seemed worth while to determine whether a similar phenomenon might not be observed with other flames. The choice of gases which will burn in one another with a flame is not great. Oxygen, fluorine and chlorine seem to be the only gases which are sufficiently powerful oxidizing agents to produce flames. While there is a large variety of oxygen flames which can be readily obtained, the choice is much more limited in the case of chlorine. With fluorine, possibly, the choice may be greater and we propose to try experiments with this gas in the near future. Of a large number of oxygen flames which we have tried, every one readily showed the D-lines. In the case of sulfur, however, the region of yellow light was confined to a very thin shell covering the inner blue cone of the flame.

### Spark Spectra in Various Gases.

The experiment described by Franck and Pringsheim,<sup>1</sup> which we have already mentioned, whereby they were able to produce the yellow light of sodium in the hydrogen-chlorine flame by sparking between platinum electrodes charged with sodium chloride, suggested that they might not have been able to obtain this effect with bare platinum electrodes: in other words, that the appearance of the D-lines in the spark might be due to the very large concentration of sodium chloride produced by the vapo-

<sup>1</sup> *Loc. cit.*

rization of the salt. This experiment was, therefore, repeated and it was found that while the sodium light was visible in the immediate neighborhood of the electrodes charged with the salt, the remainder of the spark showed little or no evidence of yellow light, although the flame contained a fairly large concentration of sodium chloride obtained by heating some of the salt in the quartz tube through which the hydrogen was passing. When bare platinum electrodes were used, no trace of yellow light could be obtained. This suggested a means of investigating the phenomenon in pure gases, thus eliminating the necessity of obtaining a flame.

The first experiments were tried with chlorine. Platinum electrodes were sealed into a Pyrex glass tube about 12 mm. in diameter, leaving a spark gap of about 3 mm. A little sodium chloride was placed in the tube beneath the spark gap and a slow current of oxygen was passed through the tube. When the sodium chloride was melted by means of a Bunsen flame, a brilliant yellow spark was obtained. The oxygen in the tube was now gradually displaced by chlorine, whereupon the yellow color of the spark changed to a pale blue. Even with a spectroscope only a faint trace of the D-lines could be obtained when the salt was heated very strongly. It was noticed that the spark passed with much greater difficulty through chlorine than through oxygen. Occasionally the spark would take a much longer path, jumping to the surface of the molten sodium chloride where it became a brilliant yellow. Various other salts were then tried in place of sodium chloride, with similar results. Thus the characteristic spectra of thallium, calcium and mercury were almost completely extinguished by chlorine.

Iodine was the next gas. In this gas the phenomenon was even more striking than in the case of chlorine. The spectra of sodium, thallium and mercury were completely extinguished, the spectrum showing nothing but the red and blue bands of iodine. Here again the spark passed with much greater difficulty through the iodine vapor than through the oxygen. This suggested a possible connection between the sparking potential in a gas and its power to extinguish the spectrum lines. In all subsequent experiments a rough measure of the sparking potential in the gas was obtained by placing, in parallel with the spark gap in the tube, an outside gap in air made of spherical polished balls of iron about 1 cm. in diameter. The distance between the balls was adjusted until the spark just failed to pass between them, taking the gap inside the tube. The ratio of this distance when the tube was filled with air and with the gas in question, was taken as a measure of the sparking potential of the gas relative to air. The accuracy of the measurements left much to be desired, the sparking distance often varying by large amounts from ex-

periment to experiment in the same gas. There can, however, be no doubt, as the following table shows, of the rough parallelism between the sparking potential, measured in this way, and the power to extinguish the spectrum lines.

TABLE I.  
Gases that show obliteration (in approximate order).

Gas.	Sparking potential (Air=1).	Metal used to obtain lines.
1. CS <sub>2</sub> .....	10	Hg, Tl
2. S.....	8	Na, Tl
3. CCl <sub>4</sub> .....	6	Hg, Tl
4. SCl <sub>2</sub> .....	6	Hg, Tl
5. As.....	6	Tl
6. I <sub>2</sub> .....	4	Na, Hg, Tl
7. SnCl <sub>4</sub> .....	10	Hg
8. Br <sub>2</sub> .....	4	Na, Tl, Hg
9. Cl <sub>2</sub> .....	3	Na, Ca, Tl, Hg
10. NO <sub>2</sub> .....	4	Hg
11. BCl <sub>3</sub> .....	4	Hg
12. PCl <sub>3</sub> .....	4	Hg
13. AsCl <sub>3</sub> .....	4	Hg
14. SiCl <sub>4</sub> .....	3	Hg
15. TiCl <sub>4</sub> .....	5	Hg
16. As <sub>2</sub> O <sub>3</sub> .....	3	Tl
17. SO <sub>3</sub> .....	3	Hg
18. C <sub>2</sub> H <sub>2</sub> .....	2	Tl
19. SO <sub>2</sub> .....	2	Tl, Hg
20. Se.....	2	Hg
21. P.....	2	Hg
22. HI.....	1.5	Hg
23. FeCl <sub>3</sub> .....	1.5	Hg

Gases that show no obliteration.

1. NO.....	1	Tl, Hg, Na
2. CO.....	1	Tl, Hg
3. H <sub>2</sub> S.....	1	Hg
4. H <sub>2</sub> O.....	1	Na, Tl, Hg
5. O <sub>2</sub> .....	1	Na
6. N <sub>2</sub> .....	1	Na
7. H <sub>2</sub> .....	1 <sup>-</sup>	Tl, Hg, Na
8. CO <sub>2</sub> .....	1	Tl, Hg
9. NH <sub>3</sub> .....	1	Hg
10. Hg.....	2/3	Tl, Na
11. HCl.....	1/4	Tl
12. HBr.....	1	Na
13. TiCl.....	1	Tl, Hg
14. HgCl <sub>2</sub> .....	1	Tl, Hg

The method of procedure, in each case, was to heat in air the substance whose spectrum was under investigation, until the spark showed the lines distinctly in a small single prism spectroscope. The lines observed were:

for mercury the green, yellow and violet lines; for thallium the green line; and for sodium the D-lines. The sparking potential was then determined as described above. It was found, in all cases, to differ very slightly, if at all, from that of air. Heating at about the same rate, the air was then gradually displaced by the vapor, such as iodine or chlorine mentioned in Col. I of Table I (preceding) p. The sparking potential was then redetermined and the effect on the spectrum noted.

### Discussion of Results.

On inspection of the table we may say, as a rough generalization, that the gases that occur toward the bottom of the table are those which, for chemical reasons, we should not expect to have the power of combining rapidly and firmly with electrons. The only powerful oxidizing agents in this part of the table are nitric oxide and oxygen. These two, however, are rather inert oxidizing agents at low temperatures. The gases that, at low temperatures, are rapid oxidizing agents, are all in the upper portion of the table. We may say, then, that a gas which is a reactive oxidizing agent has the power to obliterate the spectrum lines and has a high sparking potential. The converse, however, does not hold. Thus carbon tetrachloride certainly can not be considered as a reactive oxidizing agent. It is, however, hardly reasonable to expect that the behavior of a gas in the spark should be determined by its chemical properties at low temperatures. We should expect the compound substances in the table to be largely dissociated in the spark, and from this point of view, the effectiveness of carbon tetrachloride and the other chlorides and of carbon disulfide in obliterating the lines would be readily accounted for. At first sight, however, it is hard to explain on this basis the slight effect of hydrogen iodide and the almost complete inertness of hydrogen chloride. Two possibilities present themselves: either the emission of the spectrum lines occurs before the hydrogen iodide has had time to dissociate, or the concentration of the iodine in the completely dissociated vapor is insufficient to obliterate the lines. The following experiment was devised to decide between these two alternatives. A sealed tube furnished with a platinum spark gap was charged with hydrogen at atmospheric pressure, solid iodine in excess and a small quantity of mercuric iodide. The tube was heated to about  $158^{\circ}$  (boiling turpentine). At this temperature the vapor pressure of the iodine is approximately 0.5 atmosphere, which is about twice as great as the maximum pressure of iodine which could be obtained by the dissociation of hydrogen iodide. At this temperature both the hydrogen and mercury lines were still visible in the spark. Not until the tube was raised to the boiling point of iodine did the lines disappear completely. If we assume that the dissociation of hydrogen iodide in the spark is of the same order of magnitude as the

maximum equilibrium concentration of iodine which would be obtained by heating hydrogen iodide to infinite temperature (*i. e.*, about 0.25 atmosphere) we may conclude from this experiment that the amount of iodine liberated by the spark would be entirely insufficient to obliterate the lines. Whether the hydrogen acts merely as a diluent or has a neutralizing effect on the obliterating power of the iodine is still an open question. Hydrogen chloride and bromide are much less dissociated than hydrogen iodide, so that the entire absence of the effect in these gases is easily understood. A similar argument may be used to account for the absence of the effect in the chlorides and iodides of electropositive elements such as thallium and mercury.

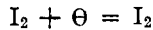
From the point of view of the theory of molecular structure of G. N. Lewis<sup>1</sup> we should expect substances such as sulfur, the halogens, nitrogen dioxide, acetylene and sulfur dioxide to combine readily with electrons. Carbon tetrachloride, however, is a completely saturated substance, as are also silicon, titanium and tin tetrachlorides and should not have this tendency. From what we have said above, however, we may account for their power to obliterate the lines if we take into account the fact that they must be very largely dissociated in the spark. The corresponding bromides and iodides would presumably behave in the same way.

Thus all gases which, according to this theory, should have a large affinity for electrons, obliterate the lines, although the converse is not necessarily true, unless we consider the possible dissociation of some of the compound substances in the spark.

These experiments throw some light on the probable mechanism of the spark. The parallelism between the power to obliterate the spectrum lines and the power to increase the sparking potential is explained if we assume that both effects are due to the same cause, namely the removal of free electrons. Let us consider what would happen as we gradually increase the difference in potential between the electrodes of a spark gap in air. As long as the potential difference is small, any free electrons present in the air due to residual ionization, photo-electric effect on the electrodes, thermionic emission or other causes will be merely swept toward the anode and removed. As the potential rises to values sufficient to impart to these free electrons the ionizing velocity, the current will increase. As the sparking potential is approached the number of electrons produced by ionization increases very rapidly until the point is reached at which the rate of production of electrons exceeds the rate at which they are removed to the anode. The condition then becomes unstable, the conductivity of the gas increases enormously and the disruptive discharge occurs. In a gas such as iodine we may suppose that

<sup>1</sup> Lewis, *THIS JOURNAL*, **38**, 762 (1916).

any free electrons which may be present would unite rapidly with the iodine molecules forming ions of large mass. Thus, for example, we might have the reaction



where  $\Theta$  represents a free electron. The heavy ions thus formed would acquire the same kinetic energy per unit distance of their path towards the anode as would the free electrons from which they were formed. If, now, these ions were capable of producing fresh ions as easily as do the free electrons, we should not expect to find any great difference between the sparking potential of a gas which united with electrons and one which did not. The observed difference in the sparking potentials of iodine and nitrogen, for example, would at once be explained, however, if the iodine ions were unable to produce ionization by collision. If we examine the experimental evidence bearing upon this point we find only two ways in which ionization has been definitely proved to be produced by bombardment of gas molecules with ions of greater mass than the electron, namely ionization by canal rays and by alpha particles. Although several observers have claimed to obtain ionization by positive rays at low voltages, their experiments, as a rule, are vitiated by failure to eliminate electrons. Horton and Davies,<sup>1</sup> in their careful work on the subject, were unable to obtain ionization by positive ions up to 200 volts, the largest voltage which they tried. It is interesting to note that the speed at which an  $\alpha$ -particle ceases to ionize air is of the same order of magnitude as the ionization speed for an electron in air. It is possible that the speed of an ion may be the factor which determines its power to ionize and not the kinetic energy, as has usually been supposed. If this is the case, it would seem impossible for an ion of even so small a mass as the hydrogen ion to produce ionization by collision in the spark.

#### Summary.

1. It was found that certain gases have the power of diminishing the intensity of the characteristic spark spectra of metals.
2. The gases which have this power have also a high sparking potential relative to air.
3. They are also, in the main, the gases which, on Lewis' theory of molecular structure, we should expect to have the power of combining readily with electrons, or which dissociate in the spark into gases of this character.
4. The parallelism between high sparking potential and power to obliterate the spectrum lines is explained if we assume that the molecules of gases which have these two properties unite with free electrons to form ions of larger mass which are incapable of producing further ionization.

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<sup>1</sup> Horton and Davies, *Proc. Roy. Soc.*, **95A**, 333 (1919).