FLAME REACTIONS OF THALLIUM.

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The terms spectra of the *first* and of the *second order* were given by Plüker and Hittorf[1] to what are known now as *band* and as *line* spectra. Mitscherlich[2] proved that the *channeling* of the band spectrum is due to the existence of a compound of a metal in the flame, while the line spectrum is produced by the elementary metal. When halogen compounds of barium are introduced in the Bunsen flame they produce their own fugitive spectra, but on dissociation in the flame they all exhibit the band spectrum of barium oxide and also the χ-line ($=5535.69$) of the metal. Mitscherlich's work points to the fact that the final spectrum produced by a halogen salt of barium is the result of a chemical change that had been undergone by the salt in question.

The well-known luminescence of a flame charged with compounds of sodium is undoubtedly due to the existence of metallic sodium in the flame. Mendeléeff[3] arrived at this conclusion from the following experiments: If hydrochloric acid gas be introduced into a flame colored by sodium it is observed that the sodium spectrum disappears, owing to the fact that metallic sodium cannot remain in the flame in the presence of an excess of hydrochloric acid. The same thing takes place on the addition of ammonium chloride, which in the heat of the flame gives hydrochloric acid. If a porcelain tube containing sodium chloride (or sodium hydroxide or carbonate), and closed at both ends by glass plates, be so powerfully heated that the sodium compound volatilizes, then the sodium spectrum is not observable; but if the salt be replaced by sodium, then both the bright line and the absorption spectra are obtained, according to whether the light emitted by the incandescent vapor be observed, or that which passes through the tube. Thus the above spectrum is not given by sodium chloride or other sodium compound, but is proper to the metal sodium itself. If every salt of sodium, lithium and potassium gives one and the same spectrum, this must be ascribed to the presence in the flame of the free metals liberated by the decomposition of their salts.

Reference has been made from time to time to the fact that free

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[1] Phil. Trans. 1885, 155.

[2] Pogg. Ann. **116**, 419 (1862); **121**, 459 (1863).

[3] "Principles of Chemistry", **1**, 563 (1891).

carbon is found in the ordinary luminous flames[1] and that the luminescence is due to this carbon. Heumann[2] pointed out that when a feebly luminous hydrocarbon flame be charged with chlorine or with bromine, the luminosity of the flame is greatly increased. The chemical activity of chlorine and of bromine brings about the separation of carbon, which, on incandescence, increases the luminosity of the flame.

While investigating the structure of luminous flames, Smithells[3] proved that free carbon is found in the luminous portion of a hydrocarbon flame. His conclusion, which is in agreement with the view of Kersten,[4] is that the separation of carbon in a flame is due simply to the decomposition of the hydrocarbon by heat. He also asserts that the glow of carbon in the luminous region is due to the heat of its own combustion, and is increased probably by the concomitant combustion of hydrogen. Smithells[5] also succeeded in precipitating copper from a flame charged with cupric chloride.

Hodgkinson[6] obtained a deposit of sulphur from a moderate-sized sulphur flame.

Bancroft and Weiser,[7] who experimented with a number of metallic salts, proved that these salts dissociate at the temperature of the Bunsen flame, of the hydrogen-air flame and of the oxyhydrogen flame, the metals being set free.

Papish[8] investigated the behavior of compounds of selenium and of tellurium in the Bunsen flame and in the hydrogen-air flame. Elementary selenium and tellurium can be easily obtained by depressing the flames with a cold object.

In all cases mentioned above the luminescense can be traced back to the existence of an elementary substance in the flame. In some cases a particular luminescence is due to the existence or formation of a certain compound in a given zone of the flame. The work described in this paper was undertaken with the purpose of throwing more light on the nature of flame reactions in general and of the reactions of thallium in particular.

Thallous Chloride in the Bunsen Flame.—"Chemically pure" thallous chloride was distilled and redistilled in a hard glass tube. The final

[1] Hilgard: Liebig's Ann. **92**, 129 (1854); Liebig's Jahresb. 1854, 287; Landlot: Pogg. Ann. **99**, 389 (1856).
[2] Chem. Centrb. 1. 1876. 801.
[3] Jour. Chem. Soc. **51**, 223 (1892).
[4] J. prak. Chem. **84**, 290 (1861).
[5] Phil. Mag. (5) **39**, 127 (1895).
[6] Chem. News **61**, 96 (1890).
[7] Jour. Phys. Chem. **18**, 259 (1914).
[8] Ibid. **22**, 430 (1918); Ibid. p. 640.

product, which consisted of fine crystals, fused to a clear liquid on heating and sublimed without leaving any residue. On examination by means of the spectroscope it was found to give the thallium line and very faint sodium lines. This salt was introduced in a hard glass tube, one end of which was drawn to a capillary and inserted in a small hole bored in the stem of a Bunsen burner. The other end of the tube was connected with the air blast. A very slow current of air was turned on, the burner was lighted, and the thallous chloride in the hard glass tube was heated to volatilization. The vapors of this salt on entering the flame imparted to it the characteristic thallium green color. On depressing the flame with a cold object, such as an evaporating dish, a metallic mirror of a brownish appearance was obtained. That this mirror was due to the deposition of thallium was proved by moistening it with a drop of hydrochloric acid and impinging a Bunsen flame on it; the characteristic green color flashed up.

Thallous Chloride in the Hydrogen-Air Flame.—Resublimed thallous chloride was placed in a hard glass tube provided with a platinum tip.
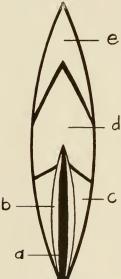

Diagram of the Hydrogen-Air Flame charged with Thallous Chloride.

a, deep green; b, almost colorless film; c, blue; d, green; e, deep green.

Hydrogen, generated from zinc and sulphuric acid and washed through a solution of silver nitrate, was passed through the tube and ignited above the platinum tip. The thallous chloride was now heated with a flattened Bunsen flame. The flame of the burning hydrogen, on becoming charged with the vapors of the thallium salt, was seen to consist of a long, slender inner cone, deep green in color, surrounded by a film which was almost colorless. The middle cone, which constituted the main part of the flame, was green for about two-thirds of its length, its lower third being blue. The outer cone, which formed the tip of the flame, was of an intense green color. The terms inner, middle and outer cones are used for the purpose of simplifying the description of the flame. Reference to the accompanying diagram will show that in practice the flame consists of five different zones, each zone having its own characteristic luminescence. On depressing the inner zone (*a*) with a cold object a lustrous dark metallic mirror of a brownish tinge was obtained. But no deposit of thallium was obtained when the part of the flame above the inner zone was depressed.

Conclusions.

Thallous chloride, when introduced in the Bunsen flame, dissociates, yielding the metal. This metal can be condensed on a cold object in the form of a brownish mirror. The characteristic luminescence of the flame is to be traced to the existence of the free metal in it.

When the hydrogen-air flame is charged with the vapor of thallous chloride, five different zones, each distinguishable by a different luminescence, can be observed. A lustrous metallic mirror of a brownish tinge can be obtained on a cold object by depressing the inner cone of the flame. The luminescence here again is to be traced to the element thallium. No deposit of thallium is obtained when the cold object is introduced in the outer zone; the luminescence in this region is undoubtedly due to the formation of an oxide or oxides of thallium.