

EFFECTS OF IONIZATION IN AN AIR-ACETYLENE
FLAME

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The occurrence of ionization of metal vapours introduced into a flame is generally known ¹). This accounts for a decrease in (atomic) light-emission as it was studied by H u l d t ²), S m i t and V e n d r i k ³). The effects of ionization in the special field of flame-photometry have been outlined by S m i t, A l k e m a d e and V e r s c h u r e ⁴) ⁵) ⁸), and have been discussed, independently, during the general discussion of the symposium of flame-photometry, U.S.A., 1951 ⁶). In this paper the results will be given of some quantitative investigations made by author with an air-acetylene flame (described in ⁵). Solutions of K and Na as chlorides in 0.15 *N* HCl were used in order to make the fractional chloride-association independent of the salt concentration, HCl being present in excess. Special measurements were made to enable correction for self-absorption of the two resonance-doublets chosen.

1. The relative emission for potassium (1–4 mg per 100 ml) was determined at heights of 10 and 23 mm respectively above the blue combustion cones centrally in the flame. The logarithmic plot of the emission versus the log of the salt concentration in the liquid, could not be brought into coincidence with the theoretical curve (derived from S a h a 's equation for constant temperature) by any parallel shifting. Moreover, both plots had different slopes, incompatible with the expected constancy of temperature and total K-concentration of the flame over that interval of height.

2. The enhancement of K-emission at flame-height of 23 mm due to sodium added at various quantities (corrected for filter-leakage, i.e. transmission of Na-light by K-filter) was measured for 1, 2 and 4 mg K per 100 ml respectively, and plotted versus the relative excess of Na. Comparison of these plots with the theoretical curves valid at the flame temperature (2500°K) should yield the absolute concentration of K-atoms + ions in the flame. However, this calculated K flame concentration divided by the K salt concentration in the solution appeared to decrease systematically by

18% with increasing salt concentration, in the investigated region.

3. A result analogous to 2. was found when K as "disturbing" element was added to Na.

4. All values of flame concentration obtained above appeared to exceed the upper limit derived from the measured properties of flame and spray, and from the salt concentration in the liquid. This upper limit fairly agrees with the flame concentration computed from the self-absorption.

As working hypotheses we assumed that:

a) the flame itself, without metal vapour, supplies already a noticeable amount of electrons;

b) this amount decreases with increasing height;

c) the upper limit of concentration stated sub 4. equals the actual concentration in the flame.

Combining a) and c) with 1., 2. and 3. respectively we obtained three separate values for the concentration of electrons proper to the flame itself (at 23 mm height). They spread about $1.1 \cdot 10^{11}$ electrons per cm^3 with a mean deviation of 30%. This agreement is satisfactory, allowing for the errors to be expected.

Hypothesis b) explains the effect of height found sub 1. It also explains the decrease in potassium (and cesium) emission with height, in contrast to sodium (being less affected by ionization), as was observed by Hasler⁷⁾ too.

It could be ascertained by blank readings that these surplus electrons do not originate from K- or Na-impurities in the flame. They may originate from the reaction zone, not being in accordance with the Saha equilibrium.

A more detailed study will be published in a near future.

Received 26-9-52.

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