INTENSITY VARIATION OF ALKALI-METAL EMISSION IN A FLAME AND EQUILIBRIUM IONIZATION ALTERATION BY A STEADY ELECTRIC FIELD

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Introduction. The effects of electric fields E on pure flames have been examined [1,2] and also on the emission and absorption of Cs, Rb, and K in air mixed with acetylene or propane-butane [3-5]. The atomic lines were attenuated near the cathode by fields of 20 to 200 V/cm for solutions at 10^{-3} M for K and Rb and 10^{-2} to 10^{-4} M for Cs. This was interpreted as due to shift to the right in the equilibrium \( \text{Me}^+ \text{Me}^- + e \rightarrow \text{Me} \) (e = electron). Similar shifts have been reported in [6,7]. Here we must consider the free-electron concentration \( c_e \) (partial pressure \( p_e \)) of the pure flame [8], which varies with the fuel gas; this is important if \( p_e \) exceeds that for the metal. Our saturation current [9] and spectroscopic [10] studies indicate that \( c_e \) is about 10^{10} cm^{-3} for an acetylene-air flame, which is much higher than for flames of air with \( \text{H}_2 \text{S} \) and \( \text{CS}_2 \) (10^6 cm^{-3}), although these have temperatures (2100-2260 K) close to those of hydrocarbon-air flames, but the latter have \( c_e \) 10^3 times as great [11]. It is to be expected that the sensitivity in flame photometry will be greater at high \( c_e \), since this will shift \( \text{Me}^+ \text{Me}^- + e \rightarrow \text{Me} \) to the left.

The cathode effect is prominent for the readily ionized alkali metals if the solutions are of concentration \( C \) about 10^{-3} M. It is of interest to examine the effects at much higher \( C \) and high \( E \), e.g., sufficient to produce the saturation current [12].

The cool plasma in the outer cone of a salt-bearing flame may be considered as an electrolyte [13] composed of metal ions and free electrons. Large amounts of metal produce high ion concentrations \( c_1 \) and also high \( c_e \). The ions are attracted to the cathode, where \( \text{Me}^+ + e \rightarrow \text{Me} \) occurs, the neutral atoms combining with components of the medium and being deposited on the cathode or remaining in the free state near it, where they may be thermally excited and so increase the intensity of the resonance line. This localization near the cathode should not only compensate the attenuation due to shift in the equilibrium but also should be independently detectable at high \( C \) and \( E \). The present tests were designed to examine this.

Apparatus and Methods. The intensity I was measured with a UM-2 monochromator working into a FEU-19M or FEU-22 photomultiplier, whose output was read by an M-95 microammeter [3, 14]. The salt solution was injected into the acetylene-air flame by a compressed-air sprayer. The cylindrical metal burner had 30 holes 0.8 mm in diameter at the exit. The appropriate part of the outer cone was focussed in the plane of the entrance slit with a short focus lens. Field \( E \) was applied by cylindrical graphite electrodes of diameter 68 mm, which were inserted in the flame about 22 mm apart. These massive electrodes were inserted directly before a measurement and did not have time to reach a temperature such as to produce thermionic emission. The burner and electrodes were adjustable at right angles to the axis of the optical system. At each set position, the current I was read with and without the field \( E \). Also, \( C \) was varied widely, as was \( E \).

Results and Discussion. Figure 1 shows the effects of \( E \) as a function of \( C \) (10^{-3} to 1.5 M) for an applied potential \( U \) of 1000 V with the electrodes 18-20 mm apart. There is a marked fall in I at 10^{-3} to 10^{-2} M for Cs and Rb, and at 10^{-4} to 10^{-2} M for K, but this is very largely suppressed at 10^{-1} M; at 1 and 1.5 M there is even some increase in I. This increase itself increases with \( E \) at high \( C \) (Fig. 2); again, the reduction in I at low C increases with \( E \) (Fig. 2b for Cs and Fig. 3 for K at 500 to 2350 V).

The nonresonant 4555 Å line of Cs shows a variation in I analogous to that for the resonant line; at \( U \) = 1500 V and \( C \) = 10^{-1} M, I is unaffected, while at 1 M increases appreciably.

The cathode field reduces I for Cs, Rb, and K only at \( C \) of 10^{-3} to 10^{-2} M, when the metal is highly ionized. The results are explained by the displacement theory and agree with the results of [3]. At higher C (10^{-2} M), the loss of I is
less pronounced, or even zero, E being the decisive feature. Here the degree of ionization is less, e.g., 75.5% for Cs at
$10^{-3}\text{M}$ [3] as against 14% at $10^{-1}\text{M}$, 39% for K at $10^{-5}\text{M}$, and 5% at $10^{-1}\text{M}$, and 52% for Rb at $10^{-2}\text{M}$ and 7% at $10^{-1}\text{M}$.

Here there are two opposing effects: the displacement weakens the atomic lines, while the neutralization tends to strengthen them. Electrolysis of the plasma will occur fairly extensively at high C and also at high E. The latter is required to produce high speeds in the positive ions near the cathode, which thus easily reach the latter and are neutralized. These neutral atoms may in part be deposited on the cathode and at once be converted to compounds, as is clear from the deposit formed on prolonged exposure to the flame. It is unlikely that some of them remain in the free state at the surface of the relatively cool cathode.

The degree of ionization falls further when C is raised to 1 M (to 1.5% for K, 2% for Rb, and ~5% for Cs), so the shift here should have a negligible effect on the atomic lines, while the electrolysis effect should be maximal, as is observed. The intensity gain is not due to the provision of extra electrical energy, since calculation shows that E would increase the energy by only about 0.1 eV.

Salt deposition on the cathode has been reported before [15, 16]; a salt-bearing flame is [16] deflected towards the cathode. This occurs for the outer cone in a pure flame. Visual observation shows that this deflection is largely independent of C and E, whereas the cathode intensification occurs only at high C and E. Hence the deflection cannot be responsible for the intensification at high C.

The widths of the cathode and anode potential-drop regions are inversely proportional to the mobilities $u$ of the positive and negative ions. The free-electron $u$ (~2500 cm$^2$/V·sec) is much greater than the cation $u$ (1-2 cm$^2$/V·sec) [17], so the cathode region is far larger than the anode one, and at high U it will fill nearly all the space between the electrodes. The observed line weakening throughout the gap in this case (Fig. 2b) is due to a shift to the right in the equilibrium consequent on withdrawal of positive ions. Surface recombination and deposition at the cathode then implies a general reduction in the free-atom concentration in the rest of the flame and hence a weaker emission.