# Letters to the Editors

Letters to the Editors on points of scientific interest related to combustion and flames are invited. The Editors do not hold themselves responsible for opinions expressed in correspondence. Anonymous-contributions cannot be accepted.

The Role of Electrons in Alkali Excitation in Flames

ELECTRONS may contribute to the excitation of alkali lines in flames according to:

$$M + e^- \rightarrow M\star + e^- \quad \dots [1]$$

$$M^+ + e^- + X \rightarrow M\star + X \quad \dots [2]$$
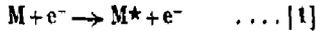
where M, M★ and M⁺ represent a ground state, excited and ionized metal atom, respectively, and X is a flame molecule. In process 1 translational energy of the free electron is converted into electronic excitation energy. In process 2 the recombination energy is partly converted into electronic excitation energy, while X carries off some of the excess energy. In flames burning at atmospheric pressure the probability of radiative recombination is small compared with three-body-recombination[1]. We want to discuss here some recent experimental data from which conclusions may be drawn about the relative importance of processes 1 and 2 in flames (outside the reaction zone) when compared with other excitation processes for the atoms (such as thermal collisions with neutral flame molecules).

Indirect evidence of the relative contribution of process 1 to the overall excitation rate may be gained from the following observations on the population of the excited metal state as measured by the method of line-reversal.

(*i*) Usually the reversal temperature of the Na *D*-doublet agrees with true flame temperature and is independent of the concentration of the sprayed Na-solution down to about 10 p.p.m. corresponding to a concentration of about 2×10^{10} Na atoms per cm³ in the flame[2,3]. These observations imply that the overall excitation rate is considerably larger than the spontaneous emission rate [M★] × A. With the stated low Na-concentration the content of free electrons in the hydrogen–oxygen–carbon dioxide flame (temperature 2 015°K) is certainly

lower than 10^{11} cm⁻³. If process 1 were the predominant one, the corresponding cross section must be at least of the order 10^{-9} cm² for electrons with kinetic energies exceeding the excitation energy, in order to explain the above result with the optical transition probability $A \approx 10^8$ sec⁻¹, and under conditions where radiation trapping is negligible[4]. Obviously, such a high cross section is very improbable.

(*ii*) In some special flames (with comparatively low collisional quenching rates for M★) the alkali reversal temperature was found to be markedly lower with low alkali concentrations (corresponding to low optical line densities) than with higher concentrations (corresponding to high optical line densities) where radiation trapping becomes important[2,4]. In these flames, which are obtained by substituting argon for nitrogen as diluent gas, the excitation rate is, at most, of the same order as the spontaneous emission rate. However, it was also found that this defect in reversal temperature again becomes independent of concentration in the range of low alkali concentrations. Consequently the overall excitation rate proves here to be independent of the free electron content (which varies with alkali concentration), which rules out the predominance of process 1.

This indirect evidence is supported by absolute rate calculations based on the absolute excitation cross section $\sigma(E)$ as a function of electron energy E, published recently by Zapesochnyi and Shimon[5] for alkali resonance lines. This function shows a steep rise to a fairly constant value σ_0 at $E \simeq E_{exc}$, where E_{exc} denotes excitation energy. We find an estimate of the excitation rate per metal atom (k_1) by electron impact, by averaging over a Maxwellian distribution of E and approximating $\sigma(E) = \sigma_0$ for $E \geq E_{exc}$ and $\sigma(E) = 0$ for $E < E_{exc}$

$$k_1 \simeq N_e \sigma_0 \bar{v}_{el} (1 + E_{exc}/kT) \exp[-E_{exc}/kT]$$

where N_e denotes electron density, $\bar{v}_{el}$ is the average electron velocity at flame temperature T, and h is the Boltzmann constant. It should be noted that equilibration of the electron energies by collisions with flame molecules is expected to proceed within a very short time interval of the order of $(m_f/m_e)\nu^{-1} \approx 10^{-7}$ sec. Here m_f and m_e are the average mass of a flame molecule and the electron mass, respectively, and ν is the collision frequency of electrons with neutral molecules ($\approx 10^{11}$ sec^{-1} in flames burning at atmospheric pressure[6]).

The overall excitation rate k_{exc} is connected through detailed balance with the overall quenching rate k_{qu} which follows from the measured yield factor p of resonance fluorescence, according to

$$k_{exc} = k_{qu}(N_1/N_0)$$
$$= (p^{-1} - 1)A(g_1/g_0)\ \exp\left[-E_{exc}/kT\right]$$

Here the fractional population (N_1/N_0) of the excited metal state is derived from the Boltzmann formula. Combining both equations we find

$$k_1/k_{exc} = N_e\sigma_0\bar{v}_{el}(g_0/g_1)(1 + E_{exc}/kT)/(p^{-1} - 1)A$$

Even in the favourable case of a hydrogen-oxygen-argon flame with $T = 2350°K$ and a measured[2,4] high p value of 0.3 we calculate for the Na D-doublet with $\sigma_0 \approx 10\text{Å}^2$, assuming a rather extreme value $N_e = 10^{13}$ cm^{-3}: $k_1/k_{exc} \approx 0.3$. Under more usual conditions the contribution of process 1 will be much smaller.

The relative importance of process 2 cannot be judged on the basis of the above observations (i) and (ii), because the excitation rate $\kappa_2 N_i N_e N_X$ (cm^{-3} sec^{-1}) can be written as $\kappa_2 K N_0 N_X$, where N_i, N_0 and N_X are the concentrations of metal ions, metal ground state atoms and flame molecules, respectively, and K is the Saha ionization constant in equilibrium. The excitation rate per ground state atom is thus independent of N_e and proportional to N_X. This process is indistinguishable, in this respect, from thermal excitation by collisions with flame molecules X.

Indirect evidence against the predominance of process 2 may be gained, however, from the observation in carbon monoxide–air flames that

deviations from Saha equilibrium due to relaxation effects (affecting the factor K in the above expression by more than $10\times$, $2\times$ and 10 per cent with Na, K and Cs, respectively) did not upset the Boltzmann equilibrium population of the first resonance lines of these metals by more than a few per cent[1].

The insignificance of process 2 in flames can also be demonstrated by comparing the rate $k_{-2}[N_i]$ of the reverse process with the overall quenching rate $k_{qu}[N_1]$ measured. A rough estimate of $k_{-2}[N_i]$ follows from the overall ionization rate $m[N_0]$ measured if we assume that a large number n of excited metal states above the ground state participate as an intermediate step in the ionization process, each of them contributing as much to the value of m as the ground state does[1,7].

Using the Boltzmann formula for N_1/N_0 we easily find

$$k_{-2} = (m/n)(g_0/g_1)\exp\left[+E_{exc}/kT\right]$$

Putting[1,7] $m = 10^2$ sec^{-1} and $n \approx 10^2$, we calculate for the Na D-doublet at $T = 2500°K$: $k_{-2} = 10^1$ sec^{-1}, which should be compared with $k_{qu} \geq 10^8$ sec^{-1} in atmospheric flames[2,4]. Using detailed balance it follows also that excitation by process 2 is negligible in ordinary flames. The situation might be different, however, for levels with $E_{exc} \approx 4$ eV.

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Quenching Diameters of Moist Carbon Monoxide–Air Mixtures

THE quenching diameter of carbon monoxide–air mixtures has been shown to depend on the moisture content.

Carbon monoxide (cylinder gas from I.C.I. Ltd) was passed through a heated tube to remove iron pentacarbonyl; it contained 0·01 per cent hydrogen (determined by GLC). Air and carbon monoxide streams were dried with phosphorus pentoxide and metered with rotameters. The moisture content of the mixed, dried streams was measured with an electrolytic phosphorus pentoxide cell and varied between 250 and 320 p.p.m. Water vapour was added to the gas streams by passing through water at different temperatures; doubling the depth of water through which the gas passed did not change the observed quenching diameter, so saturation was assumed within the limitations of the experiments.

Quenching diameters were determined by observing flashback through single holes drilled in brass plates $\frac{3}{32}$ in. thick. A flame was stabilized above the plate for one second and the gas flow stopped; this was repeated 20 times. The size of the largest hole through which the flame did not pass in 20 attempts, and the smallest size of hole to pass the flame at least once in 20 attempts, were each plotted against gas composition; minimum values were read off from these plots and the minimum quenching diameter was taken to be the mean of these. With this procedure heating of the brass plate which occurred was insufficient to affect the result.

Figure 1 shows the effect of moisture on the minimum quenching diameter. Of the five points in this figure three were obtained at a gas temperature of 25°C, one at 16·5°C and one at 35°C. If the mean quenching diameters obtained at 15·5° and 35°C are adjusted to refer to 25°C, the mean values do not move out of the ranges indicated by the vertical lines shown for each point in the figure.
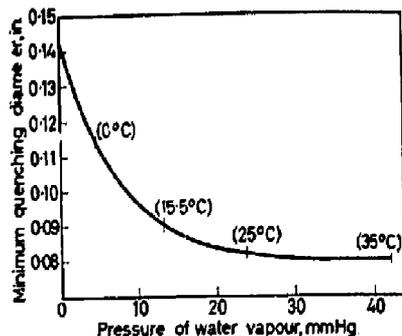

Figure 1. Effect of water vapour on the minimum quenching diameter of carbon monoxide–air mixtures. The vertical lines show the difference between the smallest diameter observed to pass the flame and the largest to quench it. Saturation temperatures are given in parentheses
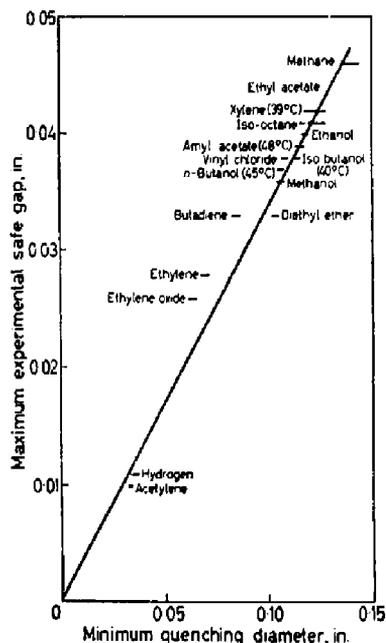

Figure 2. Minimum quenching diameter versus maximum experimental safe gap. Where quenching diameters were determined at a gas temperature other than 25°C, this is shown in parentheses

Using the same method to determine the minimum quenching diameters of 16 materials for which the Flame Proof maximum experimental