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PHOTOMETRIC MEASUREMENTS ON THE DEVIATIONS FROM THE EQUILIBRIUM STATE IN BURNT FLAME GASES

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PHOTOMETRIC MEASUREMENTS ON THE DEVIATIONS FROM THE EQUILIBRIUM STATE IN BURNT FLAME GASES

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Abstract

Photometric investigations are reported in laminar, premixed shielded flames above the reaction zone, burning at atmospheric pressure. In these $CO/N_2/O_2$ -, $C_2H_2/N_2/O_2$ - and $H_2/O_2/N_2$ - flames metal vapor was introduced. Flame temperatures ranged from 2000 to 2500°K, rise-velocities from 5 to 15 m/sec. The question is discussed as to what extent thermodynamic equilibrium does exist in (certain parts of) the flame. The meaning of (local) flame temperature and its relation to calculated adiabatic temperature and excitation temperature is considered. Complications due to suprathermal chemiluminescence and radiative non-equilibrium effects are discussed. Recombination of excess radicals causes an initial rise in temperature with height and leads to suprathermal chemiluminescence of metal lines and to continuous background radiation. Radiative non-equilibrium causes underpopulation of excited metal states and can be studied by excitation temperature measurements. From departures from metal-ionization equilibrium conclusions are drawn about the ionization mechanism, effective cross-sections and relaxation times. Chemi-ionization is also dealt with. The negligible influence of excess O-radicals in CO flames on the dissociative equilibrium makes possible to exclude particular dissociation reactions. From the measured equilibrium population of the visible alkaline-earth bands molecular excitation energies were derived and conclusions about the kind of emitters were drawn.

I. Introduction

a. Object of our Study

In this paper some deviations from the equilibrium state are discussed as they occur in the burnt gases of laminar, premixed shielded flames at atmospheric pressure. We confine ourselves here to the region above the primary reaction zone. Since these flames are produced on Meker-type burners the primary reaction zone consists of a large number of cones (in some regular array) a few mm in height.

The flames studied are $CO/O_2/N_2$, $H_2/O_2/N_2$ and $C_2H_2/O_2/N_2$ flames (sometimes Ar is used instead of N_2 as a diluent) with temperatures from 2000 to 2500°K and with rise-velocities of 5 to 15 m/sec. In the central part of these flames metal vapor is introduced by means of a liquid sprayer or by evaporating dry pure salts. The central flame part is mostly shielded by a burning mantle flame of the same gas composition, sometimes a sheath of flowing cold nitrogen is applied. Both sheaths prevent infusion from the environment and promote homogeneity over the flame cross-section.

The subjects discussed here form part of the program of the Flame Research Group of the State University of Utrecht.(1-8)

b. Equilibrium

Before discussing deviations from the equilibrium state we first define general thermodynamic equilibrium as follows: A volume of gas is said to be in thermodynamic equilibrium at the temperature T, when this temperature suffices to describe(9,19)

(i) the radiation density in the volume (according to Planck's radiation formula)
(ii) the distribution of energy in the internal and external degrees of freedom of the gas (according to the Maxwell-Boltzmann formula)
(iii) the degrees of ionization and dissociation (according to Saha's formula and the law of chemical equilibria).

Only if these requirements are fulfilled has the temperature T a unique meaning.

In order to answer the question of equilibrium experimentally many investigators have determined the "temperatures" that correspond to different aspects of the flame, e.g., the velocity distrubution of the particles and the population ratio of the various energy levels of the particles. The better these temperatures coincide, the better the state of equilibrium, and the more physical meaning the "temperature" of the flame possesses. To avoid confusion the temperatures are named after the special processes to which they apply, e.g., translational temperature, excitation temperature, etc. These temperatures appear to coincide gradually in the sequence: translational, rotational, electronic, vibrational, dissociation and ionization temperature. The radiation temperature forms an exception (cf. Sec. IV).

Let us see to what extent general thermodynamic equilibrium does exist in our flames. The attainment of equilibrium within any enclosed system requires time. It cannot be expected a priori that in a flame the establishment of equilibrium is sufficiently rapid to give no considerable deviations in any part of the flame (2,6). In the first reaction zone considerable deviations from equilibrium do exist, since here the chemical energy suddenly released by oxidation of the fuel gases is not yet equipartitioned among the various degrees of freedom. But also in the flame body two kinds of deviations from general thermodynamic equilibrium have to be considered.

(i) generally the temperature is locally different throughout the flame body
(ii) at a given locus in the flame the various forms of energy may not be equilibrated among one another

Ad (i): Even in the body of premixed, laminar flames differences in temperature may be expected. The combustion reaction causes a rapid rise of the flame temperature and nearly this whole rise takes place in the (relatively thin) reaction zone. The concentrations of the major stable flame species, such as CO_2, H_2O, N_2, etc., when leaving the reaction zone are not much different from their equilibrium values. But the radicals leave this zone with concentrations exceeding markedly their equilibrium values. Above the reaction zone these radicals recombine slowly to stable molecules and consequently the flame gas mixture approaches gradually to a complete chemical equilibrium state.

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Because of the energy released in the radical recombinations the temperature is further enhanced. On the other hand radiative losses and heat losses to the burner are also present. The two effects combined cause the flame temperature to reach a maximum as a function of rise-time and to decrease afterwards. One cannot speak of general thermodynamic equilibrium, since there is a net transport of heat, radiation and mass through the flame. If the rate of transport is slow compared to the rate at which the energy is equipartitioned over its different degrees of freedom, at a given locus, we still may speak of a local equilibrium characterized by a local temperature.

It should be noted that the radical concentrations may approach closely their equilibrium values in the region downstream the maximum of temperature, but a full equilibrium state is never reached. For the equilibrium values themselves shift continuously with increasing height because of varying temperature, so that there is always a lag behind the local equilibrium state due to relaxation effects.

Ad (ii): In the discussion as to what extent the energy is equilibrated at a given locus in the flame, one must take into account the fact that the flame gases have rise-velocities ranging from 5 to 15 m/sec. The energy released in the reaction zone must be redistributed after subsequent collisions among the flame components. Establishment of thermodynamic equilibrium requires that the particles have suffered a sufficient number of collisions with each other and this takes time. In flames at atmospheric pressure a flame molecule makes about 10^6 - 10^7 collisions per msec with the surrounding molecules(2,6,20). The flame gases cover a distance of 5-15 mm from the reaction zone upwards within 1 msec. To what extent will equilibrium be attained within this time-interval?

The equilibration of the translational and rotational degrees of freedom is practically immediately established(2,6,9,20). The equipartition over the vibrational degrees of freedom proceeds more slowly(20-22). A serious lag in this equipartition is not to be expected in our flames(2), neither with the higher nor with the lower vibrational levels(23). One may ask whether deviations from molecular dissociation equilibrium would occur. As we will discuss below (cf. Sec. II) the theoretical and calculated flame temperature agree very well. This justifies the assumption that the majority of the flame molecules are present in equilibrium concentrations(2,9,20).

Concerning the equilibrium ionization in normally burning, non-sooting, metal-free flames we may refer to the many publications dealing with excess ionic and electronic species found in and above the reaction zone(20,24,25,26). These excess charged species are probably formed in the reaction zone of hydrocarbon containing flames and they recombine beyond this zone. In pure CO and H_2 flames no electrons or ions could be detected(6,25). Deviations from the metal ionization equilibrium will be discussed in Sec. V.

Since a flame is not a black-body (It lacks walls at equal temperature with the flame gases), radiative equilibrium cannot exist. The radiation emitted by the flame gases is not compensated for by absorption of an equal amount of radiation from the surroundings. This outward radiation leak leads to a (sometimes measurable) effect of depopulation of the higher energy levels of the particles with respect to their lower levels. Only for strong resonance lines (at the center of these lines) may we expect that radiation equilibrium exists, at least in the interior part of the flame. The underpopulation of the excited levels thus depends on the metal concentration in the flame. The flame temperature derived from line-reversal measurements (= excitation temperature) will consequently be lower than the translation temperature (cf. Sec. II). Noticeable effects will only occur at low metal concentrations when the diluent gas is monatomic(2,9,16) (cf. Sec. IV).

From the survey given, it follows that in the flame no general thermodynamic equilibrium exists. We will therefore use the term "thermal equilibrium" for the state of the gases in which the distribution of the velocity of the particles and the population of their energy levels can be described by a single value of T. In the major part of our flames such a thermal equilibrium state is attained fairly closely (See below).

II. The Flame "Temperature"

Although there is no reason a priori to prefer one temperature to another, the translational temperature, deduced from Maxwell's formula for the velocity distribution of the particles, is often considered the most true temperature from which the others may deviate. The reasons are that the kinetic energy is very soon equipartitioned (See above) and that there is only one translational temperature(9) (as opposed to the various excitation temperatures). In the following what we mean with "temperature" of the flame is the translational temperature.

From the enthalpy of the initial gases and the reaction products, and from the specific heat of the latter together with the equilibrium constants of the dissociation equilibria, the adiabatic temperature of the burnt gases can be calculated(9,27). The necessary constants are provided by chemical tables. The calculated flame temperature should equal the measured temperature of the flame, provided that equilibrium prevails in (that part of) the flame and that one corrects for energy losses(9).

Many methods are available for measuring the flame temperature. Yet the method of "line-reversal" which determines essentially the excitation temperature has to be preferred(9,19). The choice of this measuring method is based upon avoiding of two sources of systematic error(9).

(i) The flame "temperature" should approach as close as possible the translational temperature, which is certainly well established. So one prefers the measurement of a "temperature" that is fast in equilibrating with the translational temperature.

(ii) The method of measurement itself may introduce errors, due to self-absorption, insufficient resolving power of the dispersing system, non-linearity of the detection device or errors of calibration.

As is discussed in detail by Snelleman(9,19), the method of line-reversal seems to meet the demands and this method is chosen for the measurement of flame temperature.

Since the application of this method essentially requires that the population of higher and lower level of the atomic line involved agree with the Maxwell-Boltzmann formula, complications may occur due to two processes:

(i) Chemical non-equilibrium, i.e. supra-thermal chemiluminescence, which effect causes an overpopulation of the upper level of the line, may in some cases lead to a too high measured excitation temperature (cf. Sec. III).

(ii) The radiative non-equilibrium (See the above) may result into an underpopulation of the excited metal states. When the yield-factor for resonance fluorescence (defined as the fractional possibility that an excited atom looses its energy by photon-emission) is relatively high, large differences between translational and excitation temperature may be found (cf. Sec. IV). Then the excitation temperature is found too low compared with the translational temperature.

Some other possible errors occurring in using the line-reversal method are: excitation lag (can be neglected in our flames) and self-reversal (can be avoided by using shielded flames).

Snelleman in our laboratory, using a photo-electric line-reversal method, obtained with his apparatus an accuracy of ± 1°K and a reproducibility of the temperature in his flame of ± 2°K. He reported the following results for the reversal temperature of various spectral lines (in the same flame)(9).

TABLE 1. REVERSAL TEMPERATURES OF VARIOUS SPECTRAL LINES

Element	Wavelength(Å)	Radiation Temp. of Strip Lamp(°K)
Lithium	6708	2432 ± 2
Sodium	5890	2435 ± 1
Potassium	7665	2436 ± 1
Rubidium	7948	2436 ± 1

The number of lines used and the temperature measured are a strong indication that thermal equilibrium prevails in the flame within 2°, at least up to excitation energies of about 2 eV. (The corrections for the effect of radiation leak may be neglected under the experimental conditions used here).

The flame temperature can also be calculated under assumption of an equilibrium state, when one knows the heats of formation at 298°K of the initial components, the heats of formation at 298°K and the specific heats from 298°K to the flame temperature of the final components, and the constants of the dissociative equilibria occurring in the burnt mixture. Since these calculations are laborious a digital computer was used(19,27). It should be remarked that with the same programs the equilibrium composition of the burnt gases at each locus in the flame can be calculated from the supply of unburnt gases and the (measured) local flame temperature.

In the next figure a comparison is shown of measured (reversal) and calculated (adiabatic) temperature in an acetylene - air flame.

One sees that the agreement between calculated and measured temperature is very good, a nice confirmation for the correctness of calculation and measuring methods and for the existence of thermal equilibrium in our flames.

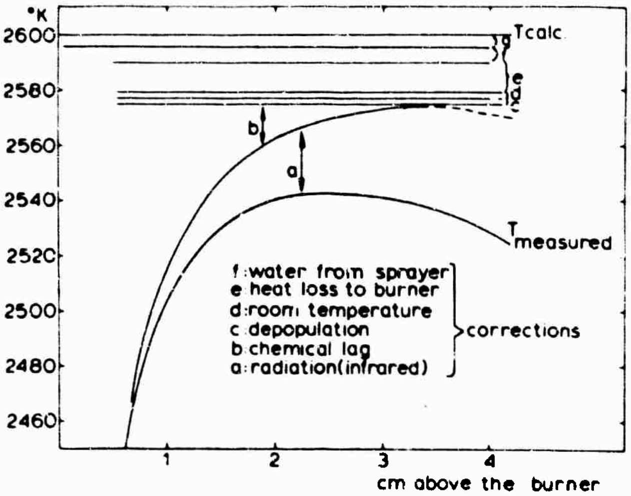

FIGURE 1. A composite graph of the various steps in the comparison of measured and calculated temperatures. Corrections: a: radiation loss between burner top and height of measurement. b: incomplete equilibration of the gases. c: difference between gas and measured excitation temperature. d: effect of room temperature on flame temperature. e: net heat loss to the burner (conduction and radiation, minus heat restored to the flame). f: cooling effect of water sprayed into the flame. The remaining discrepancy (g) may be ascribed to the difference between the temperature scales; i.e. Thermodynamic Temperature Scale and International Practical Temperature Scale (Courtesy of Dr. W. Snelleman).

III. Chemical Non-Equilibrium Due To Slow Recombination of Excess Radicals

As stated above in the reaction zone H, OH and O-radicals are formed in excess over their equilibrium values(15,28,29). So the burnt gas mixture above the cones is not in chemical equilibrium, but it will approach gradually to equilibrium with increasing rise-time. Although chemical equilibrium does not exist, there occur fast binary reactions as a result of which the radical concentrations are related to the concentrations of some of the molecular species in the same way as under equilibrium conditions(29). These fast reactions will be referred to as "partial equilibria". They cause no decrease of the total radical concentration(29). So equilibrium can only be established by radical recombination reactions, which (mostly) include slow ternary reaction steps.

Bulewicz, James and Sugden have given a theoretical treatment of the way in which radical recombination occur, especially in oxygen-lean $H_2/O_2/N_2$(28). Zeegers in our laboratory has made a more general approach and has extended this treatment to CO - and C_2H_2 - flames with different gas composition(12,15). He took also into account: decay of O-radicals through the reactions $CO + O \rightarrow CO_2$ and $O + O \rightarrow O_2$; variation of the concentrations of H_2, O_2 and CO by radical recombination and the production of radicals by thermal dissociation of H_2, H_2O, CO_2 and O_2 and the effect of varying temperature upon the rate of the dissociation reactions and upon the bulk flame gas composition.

The following recombination reactions are considered:

$$H + H + M \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} H_2 + M^* \qquad (I)$$

$$H + OH + M \underset{k_2}{\overset{k_{-2}}{\rightleftarrows}} H_2O + M^* \qquad (II)$$

$$CO + O + M \underset{k_3}{\overset{k_{-3}}{\rightleftarrows}} CO_2 + M^* \qquad (III)$$

$$O + O + M \underset{k_4}{\overset{k_{-4}}{\rightleftarrows}} O_2 + M^* \qquad (IV)$$

(M is third body necessary to carry off the reaction energy released).

The following partial equilibria are established in our flames for 99% within 10^{-5} to 10^{-6} sec, so that one may conclude that these relations are valid in any place in the flame, although the ratio of actual concentration over equilibrium concentration of a flame constituent may vary with height.

$$H_2 + OH \rightleftarrows H + H_2O \qquad (V)$$

$$H_2 + O \rightleftarrows H + OH \qquad (VI)$$

$$O_2 + H \rightleftarrows O + OH \qquad (VII)$$

$$CO + OH \rightleftarrows H_2 + CO \qquad (VIII)$$

(with equilibrium constants K_5 . . . . . K_8).

It is possible to measure directly [H] and [OH] as a function of rise-time by making use of photometric measurements(12,15). For [O] this is not easily possible.

a. Derivation of [O] from the Initial Temperature Increase

In (dry) CO-flames two recombination reactions may be responsible for the initial rise of flame temperature, namely reactions (III) and (IV). As is proved in detail by Zeegers in our flames reaction (III) is the predominant one(15).

If the temperature rise is not effected by heat losses, the temperature T_t as a function of rise-time, t, will reach asymptotically and monotonously a final value, T_e, while $[O]_t$ approaches with increasing t its equilibrium value $[O]_{eq}$. One has the following equation(30,15).

$$Nc_p(T_e - T_t) = q([O]_t - [O]_{eq}) \qquad (1)$$

Here N is the total number flame molecules per cm^3, c_p is the average specific heat at constant pressure of burnt gases in cal mol^{-1} $^oK^{-1}$, q is the heat released by recombination of one gram atom O with one gram molecule CO in cal mol^{-1} and concentrations are expressed in cm^{-3}.

Two subjects have to be discussed before deriving the O-concentrations from the measured temperature.

(i) The measured local Na- line-reversal temperature may locally deviate from the true translational temperature because of suprathermal chemiluminescence. The excitation of metal atoms in flames occurs mainly by conversion of vibrational energy into electronic excitation energy in collision with molecules such as N_2, CO and CO_2. Excitation partly occurs by chemiluminescence (See below). When chemical equilibrium is fully established in the flame, chemiluminescent reactions do not disturb the thermal population of an excited state ("thermal chemiluminescence). However, when the radicals are present in excess concentrations, overpopulation of an excited state is feasible ("suprathermal chemiluminescence). The relative degree of overpopulation depends also on the flame temperature. i.e. on the thermal excitation rate by collision of the 1st kind. Even in flames with the lowest temperature (i.e. with the relatively highest contribution of suprathermal chemiluminescence) suprathermal chemiluminescence of the 3P state of Na and the 2P state of Li could be ruled out. This appears not to hold, however, with excited states in the order of 4eV above the ground-state, as will be shown for the blue K-doublet at 4040Å (See below).

The absorption and the emission of the Na and Li resonance lines were measured as a function of rise-time. The curves of the ground-state concentrations measured coincide exactly with the curves computed from emission curves and line-reversal temperature. So both populations are in thermal equilibrium and suprathermal excitation is negligible with both doublets.

(ii) We assume that the initial increase in flame temperature is only due to the recombination of CO + O. This assumption has been checked quantitatively in H_2 - and C_2H_2 - flames, where the radical concentrations involved can be determined independently of the temperature rise(15). The results confirm our assumption very satisfactorily.

From Eq.(III) we derive

$$\frac{-d[O]_t}{dt} = k_3^M [M][CO][O]_t - k_{-3}^M [M][CO_2] \qquad (2)$$

Taking into account that: $k_3^M [M][CO]_{eq}[O_{eq}] = k_{-3}^M [M][CO_2]_{eq}$ if $T \simeq T_e$, that [CO] is practically constant, so that $[CO]_t \simeq [CO]_{eq}$ through the whole flame and that the same holds for $[CO_2]$ we find from Eq. (2)

$$\frac{-d[O]_t}{dt} = k_3^M [M][CO]_{eq} \left\{[O]_t - [O]_{eq}\right\} \qquad (3)$$

Considering that k_3^M [M] is practically independent of T and after putting $[O] = [O]_i$ at t = 0, we get

$$[O]_t - [O]_{eq} = \left\{[O]_i - [O]_{eq}\right\} \exp\left\{-k_3^M[M][CO]_{eq}\cdot t\right\} \qquad (4)$$

By substituting this expression in Eq. (1), T_c-T_t is found as a function of t, according to

$$\frac{Nc_p}{q([O]_i-[O]_{eq})}(T_e-T_t) = \exp\left\{-k_3^M[M][CO]_{cq}\cdot t\right\} \qquad (5)$$

The values of T_e - T_t, i.e. the temperatures corrected for radiation losses may be found from the experimental T_r - versus-t curve by extrapolation(9,6,15). This procedure is presented in figure 2 for a CO-flame.

From the straight line obtained in Fig. 2b it appears that the assumption concerning $k_3^M[M][CO]_{eq}$ is justified. The intercept with the ordinate axis of the curves yields the initial O-concentration, $[O]_i$, in absolute measure, according to $[O]_i$-$[O]_{eq} = \frac{Nc}{q}p$ $(T_e$-$T_i)$, where T_i is temperature at t = 0. From the known values of $[O]_i$ and of $(T_e$-$T_t)$ one calculates now readily $[O]_t$ for any value of t. From the slope of the curves and the known values of $[CO]_{eq}$ the following values of $k_3^M[M]$ were derived(15): $k_3^M[M] = (2.7 \pm 0.3) \times 10^{-15}$ $cm^3 sec^{-1}$ and $(2.2 \pm 0.3) \times 10^{-15} cm^3 sec^{-1}$ for the CO-flames, respectively.

It should be remarked that the actual concentrations of O-radicals and of the other flame constituents can be calculated, when the actual values of [H] and [OH] are known, using the four equilibrium relations and the mass balances(15).

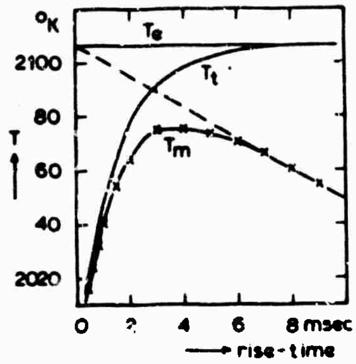

FIG. 2a Measured temperature T_m is plotted as a function of rise-time for a CO-flame. T_t is temperature corrected for radiation losses by means of linear extrapolation. T_e is final temperature at full chemical equilibrium, corrected for radiation losses. (Courtesy of Dr. P. Zeegers).

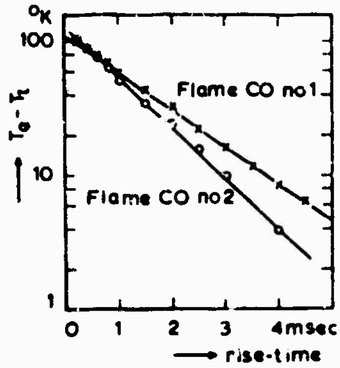

FIG. 2b Difference between final equilibrium temperature, T_e, and measured local temperature, T_t, corrected for radiation losses as a function of rise-time for two CO-flames.

b. Suprathermal Chemiluminescence of OH and blue K-doublet.

In the flames discussed the excitation, deactivation and radiation of an atom or molecule may be described by the chemiluminescent reactions I-IV and the following two reactions:

$$X + M \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} X + M^* \qquad (IX)$$

$$\text{and } h\nu + M \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} M^* \qquad (X)$$

where M stands for the electronic ground-state particle to be excited and M^* for K in the S ^2P state or for OH in the excited state $^2\Sigma(v' = 0)$ emitting radiation in transitions to the ground state $^2\Pi(v'' = 0,1,2,$ etc.) through process (X), and X is a flame molecule.

If self-absorption is negligible the total emission, J, expressed in quanta cm^{-3}sec^{-1} is given by(13,15)

$$J = p[M] \left\{ E[H][OH] + k_5[X] \right\} \qquad (6)$$

Here

$$E = [M]\left\{ k_2 + k_1 K_5 \frac{[H_2]}{[H_2O]} + k_3 \frac{K_5}{K_6 K_8} \frac{[CO_2]}{[H_2O]} + k_4 \frac{K_5 K_7}{K_6} \frac{[O]_2}{[H_2O]} \right\} \qquad (7)$$

and p (the yield factor of resonance fluorescence) = $A / k_{-6} + Z$. Here A is the transition probability and Z is the number of effective quenching collisions per sec, which equals:

$$k_{-1}[H_2] + k_{-2}[H_2O] + \text{- - - - - - -} + k_{-5}[X]$$

(cf. reactions I-IV, and IX).

The intensity of the thermal emission J is given by Eq. (6) in which [H] and [OH] are substituted by the corresponding equilibrium concentrations (Eq. (6s)) J_{th} follows also from the Boltzmann equilibrium distribution and the Einstein Transition probability according to

$$J_{th} = \left\{ g \cdot A[M] \exp\left(-E_{exc}/kT\right) \right\} / Q \qquad (8)$$

where Q, g and E_{exc} are partition function, statistical weight-factor of upper level, and excitation energy respectively. [M] is supposed to equal the total concentration of species M.

One finds for the suprathermal chemiluminescent emission

$$J_{ch} = J - J_{th} = p[M]\, E \left\{ [H][OH] - [H]_{eq}[OH]_{eq} \right\} \qquad (9)$$

The quantities occurring in Eq. (9) can be found from experiments and calculation, except for the factor pE. The relation between J_{ch} and $\left\{[H][OH] - [H]_{eq}[OH]_{eq}\right\}$ can be checked experimentally and the absolute value of pE can then be found One plots the experimental values J_{exp} in relative measure logarithmically versus the rise-time. The thermal emission is known in absolute value from Eq.(8) and is also plotted in the same graph. The J_{exp}-curve is now shifted along the intensity axis into such a position that the ratio $(J_{exp} - J_{th})_1 / (J_{exp} - J_{th})_2$ at two extreme heights h_1 and h_2, corresponding to rise-times t_1 and t_2, respectively, fitted in with the ratio predicted by Eq. (9) from the known radical concentrations at these two heights. Then J_{ch} is known in absolute measure as a function of rise-time.

In figure 3 some results for the (0-0) band of OH are given.

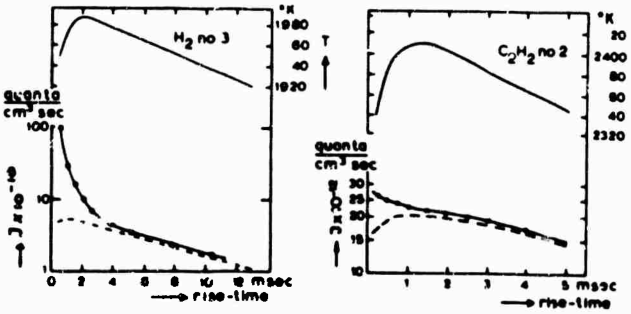

FIG. 3. The OH-emission at 3064Å is plotted in absolute measure versus rise-time for H_2 - and C_2H_2 - flames. The dashed curves present the corresponding thermal OH-emission as calculated from temperature

and (known) OH-content. The two distinct points (•) indicate the heights h_1 and h_2, in which both curves are adapted. (Courtesy of Dr. P. Zeegers).

In figure 4 J_{ch}/[OH] is plotted versus $\{[H][OH] - [H]_{eq}[OH]_{eq}\}$ for both flames.

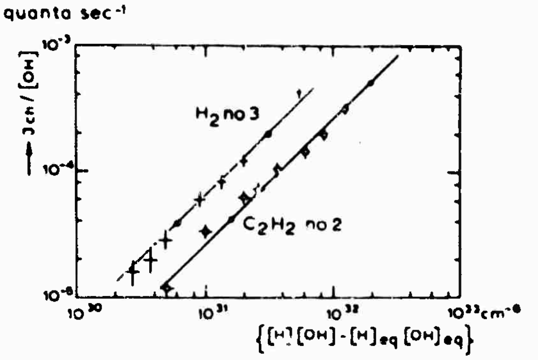

FIG 4. Suprathermal chemiluminescent emission of OH at 3064Å per OH-radical, as a function of the product of excess radical concentrations. (Courtesy of Dr. P. Zeegers).

The experimental points appear to fit very nicely a straight line through the closed circles (See above), which confirms the chemiluminescent mechanism proposed. From the intercept of the curves one finds pE-values for each flame. Since the relevant p-values are known from Hooymayers'(17) measurements (See Sec. IV), E-values could be found for three $H_2/O_2/N_2$ and one $H_2/O_2/Ar$ flame.

From this E_{OH} value Zeegers(15) derived a mean value for k_2 equal to (7 ± 1) x 10^{-33} cm^6sec^{-1} at temperatures in the range 1911-2018°K. Kaskan has reported a value of 3 x 10^{-32} cm^6sec^{-1} at 1900°K(31) This value can be recalculated (by using more recent values for A and p) to (10 ± 3) x 10^{-33} cm^6sec^{-1}.

The results in C_2H_2-flames cannot so easily be interpreted and do not lead to definite values of specified rate constants(15).

In the same way the chemiluminescence of the 4044/47Å doublet of K was measured in H_2-flames. A complication arises here with respect to the increase of flame background as a result of the reaction K + OH → KOH + hν(15). Results are shown in figure 5.

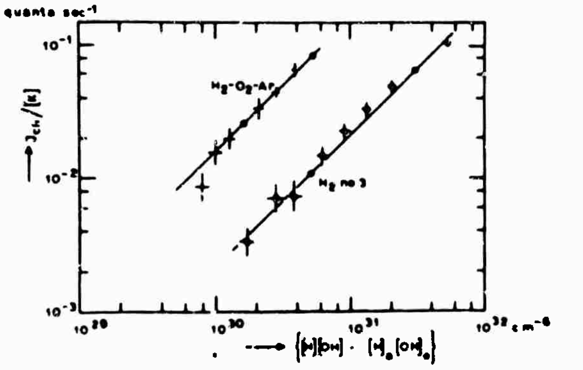

FIG. 5. The suprathermal chemiluminescent emission of the blue K-doublet is shown in two H_2-flames. Closed circles present points used in the adaptation of (relative) experimental and (absolute) thermal emission curves. (Courtesy of Dr. P. Zeegers).

Also in these measurements the proposed reaction mechanism is clearly confirmed. From these measurements an average value of k_2^K equal to (3.5 ± 0.3) x 10^{-30} cm^6sec^{-1} can be derived.(15). In the C_2H_2-flames similar difficulties as with OH (See above) show up.

From the results given we may also conclude, that reaction (II) is the predominant reaction in the chemiluminescent excitation of OH and K in H_2-flames. In the C_2H_2-flame reaction (II) is also the most important, but here reaction (III) contributes to the chemiluminescence too. The reactions (I) and (IV) can be neglected in this respect.(15)

Recently Carabetta and Kaskan(32) have measured the chemiluminescence of Na in H_2, CO/H_2 and CO - flames. Their measurements refer to the reaction zone of low-pressure flames at T ~ 1500°K. They found that the reaction O + O + Na (k ~ 1 x 10^{-29} $cm^6mol^{-2}sec^{-1}$) was predominate, followed by H + H + Na (k ~ 4 x $10^{-31}cm^6mol^{-1}sec^{-1}$).

c. Contribution of Suprathermal Chemiluminscence to the Flame Background

The study of flame background may yield information on radical recombination. Only the continuous background will be considered here. When radicals recombine the stabilization of the association complex may also take place by radiation. This radiation is a true continuum, but it occurs at wavelengths longer than a certain cut-off wavelength that is connected with the available chemical reaction energy.(15)

Several recombination reactions that may give rise to continuum radiation have been reported. Zeegers did some crucial experiments(14,15) which led to the conclusion that continuum emission is completely absent in H_2-flames. This is consistent with Dean and Stubblefield(33), but not with Padley(34). From these measurements one may conclude that the background emission in CO- and C_2H_2-flames is only due to the reaction CO + O + (M) → CO_2 + (M) + hν. (We do not want to go into details with the implication involved in this reaction. It is discussed elsewhere(15,35).

The background emission in CO- and C_2H_2-flames was photometrically measured, especially its dependence on temperature, on CO and O-concentration and on wavelength was investigated. Absolute intensity calibration was made by comparing the flame background with the emission of a calibrated tungsten strip lamp.

The explicit dependence of the background emission on CO- and O-concentrations was found by using a procedure similar to that used in Section IIIb. In figure 6 some results are shown

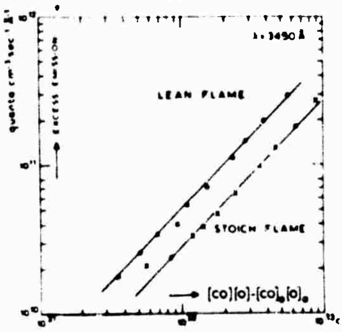

FIG. 6. The excess background radiation (in absolute measure) is plotted as a function of the excess

CO-and O-concentrations for two C_2H_2-flames (Courtesy of Dr. P. Zeegers).

The same result has been found at several other wavelengths in the range from 2300 to 6000 Å. This confirms the reaction mechanism proposed. The radiation originates from excited CO_2^* states that are populated from ground state CO_2 molecules by thermal collisions with flame molecules, as well as by recombination of CO and O. Close to the reaction zone the latter process may dominate, because CO and O are present in excess over their equilibrium concentrations. As larger heights the background emission approaches fairly well its equilibrium value which depends on T according to $\exp[-h\nu/kT]$ (14,15).

IV. Radiative Non-Equilibrium in Flames

Infrathermal population of excited levels occurs because of a deficiency of radiative excitation. This deficiency exists when the radiation density in the flame is lower than that of a black-body at flame temperature.

Deactivation of an excited state occurs by quenching collisions and by emission of radiation, excitation occurs virtually by collisions of the first kind only, at least with low metal concentrations where the radiation density of the metal line is low when compared to Planck radiation. The question which form of energy the electronic excitation energy is converted into or supplied from, is discussed in detail elsewhere(2,6,20). The conversion of vibrational energy seems to be favored, since here are no restrictions resulting from conservation of linear and angular momentum (cf.Sec V).

The degree of underpopulation of an excited level can be easily expressed by introducing the yield-factor p (16,17). We have $p = A/k_{-5} + A$, where k_{-5} describes the probability per sec. that the excited atom loses its energy in a quenching collision with a flame particle. (See above).

At low radiation density (≈ low metal concentration) we find the relation between the actual ($=N_1$) and the theoretical ($=N_1^0$) number of atoms in an excited level as (17)

$$N_1/N_1^0 = 1-p \qquad (10)$$

Because of the effect of radiative non-equilibrium on the occupation of the excited state the line-reversal temperature, T, will differ by an amount ΔT_L from the true temperature, T_t. At low metal densities it holds that

$$\Delta T_L = \frac{kT_t^2}{h\nu_0} \ln(1-p)^{-1} \Big/ \left[1 + \frac{kT_t}{h\nu_0} \ln(1-p)^{-1}\right] \sim \frac{kT_t^2}{h\nu_0} \ln(1-p)^{-1} \qquad (11)$$

since for all relevant p-values in our flames

$$\frac{kT_t}{h\nu_0} \ln(1-p)^{-1} \ll 1.$$

It can further be shown that in the case of combined Lorentz and Doppler broadening, that occurs with the alkali lines in the flame, the deviation ΔT in line-reversal temperature approaches zero as $N_0^{-\frac{1}{2}}$ at very high density (N_0 = concentration of ground state atoms)(17). This asymptotic behavior enables us to find the true flame temperature by extrapolation from the reversal temperature measured at high concentrations.

When measuring reversal temperatures when the atomic density varies from small to large values, we are able to derive or to check the yield-factor p (See Eq. 11).

When the metal atoms undergo quenching collisions in a mixture of flame molecules of different species the quenching frequency k_{-5} $(= A\frac{1-p}{p})$ is given by(17)

$$k_{-5} = \sum_j n_j \, (Q_{qu})_j \left\{ \frac{8kT}{\pi} \left(\frac{1}{m_{at}} + \frac{1}{M_j}\right) \right\}^{\frac{1}{2}} \qquad (12)$$

Here n_j is the number of particles (in cm^{-3}) of the j^{th} flame gas component with molecular mass M_j, ($(Q_{qu})_j$ is here temperature dependent).

The value of p can be measured in actual flames by means of resonance fluorescence, i.e. the flame containing e.g. Na-vapor is irradiated by a Na-discharge lamp. One may determine p by measuring the ratio of the total flux of the fluorescent radiation to the primary radiation flux that is absorbed in the flame. (For experimental procedure: cf. lit. (17,18).

When determining p in flames with different qualitative and quantitative gas composition, it is possible to derive the specific quenching cross-sections of metal lines for the different flame gas molecules and atoms. Also the temperature dependence of these cross-sections can be found(17,18).

Hooymayers at our laboratory determined in this way the cross-sections of the Na D-doublet, the red and blue resonance doublets of K and the OH-band (at 3064 Å) for the different flame gas components(16,17). From his results it appeared that atoms are not effective in quenching (Q_{qu} ~ 1-4 Å^2). The most effective quenchers are the di- and tri-atomic molecules. Some specific Q_{qu} values for the Na D-doublet at T = 2000 °K are(17)
$Q_{qu}(Na - N_2) = (28 \pm 2)$ Å^2; $Q_{qu}(Na - CO_2) = (94 \pm 3)$ Å^2;
$Q_{qu}(Na - H_2) = (15 \pm 0.5)$ Å^2; $Q_{qu}(Na - O_2) = (62 \pm 2)$ Å^2;
$Q_{qu}(Na - CO) = (70 \pm 3)$ Å^2; $Q_{qu}(Na - Ar) = (2.3 \pm 0.1)$ Å^2
and $Q_{qu}(Na - H_2O) = (1.0 \pm 0.06)$ Å^2. The low value for H_2O should be noted. Some specific cross-sections (at T = 1800 °K) for the OH-band are(17):

for O_2 :(10 ± 2) Å^2, for H_2O :(37 ± 6) Å^2 and

for N_2 :(7 ± 1) Å^2. Here H_2O is much more effective in quenching than with the alkali atoms (See for further details lit. (17)).

From Hooymayers' work it appears that the Q_{qu}-values for the diatomic molecules H_2, N_2 and O_2 show a pronounced dependence on the resonance defect ΔE (= difference between the alkali excitation energy and the nearest vibrational level). Large Q_{qu}-values are associated with small energy defects(17). Furthermore the temperature dependence of Q_{qu} is given by $Q_{qu} \propto T^{-1}$.

The experimental results with Na agree reasonably well with data obtained in vapor bulbs, shock tubes and excitation by sparks(17,18,36,37). The values reported by Jenkins(39) in a flame at 1800 °K are systematically lower by a factor 2. No explanation for this discrepancy can as yet be given. It should be remarked here, however, that Hooymayers' p-values derived independently from line-reversal temperatures are nicely consistent with the data obtained from fluorescence measurements. Finally, we may note that the cross-section values reported by Carabetta and Kaskan(32) seem to agree with Hooymayers' results within 20%.

From the measured cross-sections one readily concludes that indeed the activation and deactivation of excited levels occur predominantly in inelastic collisions with molecules in which vibrational energy is converted into or supplied from the electronic excitation energy.

When the specific cross-sections and their temperature dependence are known, one is able to calculate the p-factor for a flame of which the temperature and the composition of burnt gases are determined. Therefrom one may readily derive the value of ΔT_L. Conversely from the measured value of ΔT_L one may compute the p-value (See below).

In the next figure the measured Na-line-reversal temperature is plotted as a function of the Na-content in the flame.

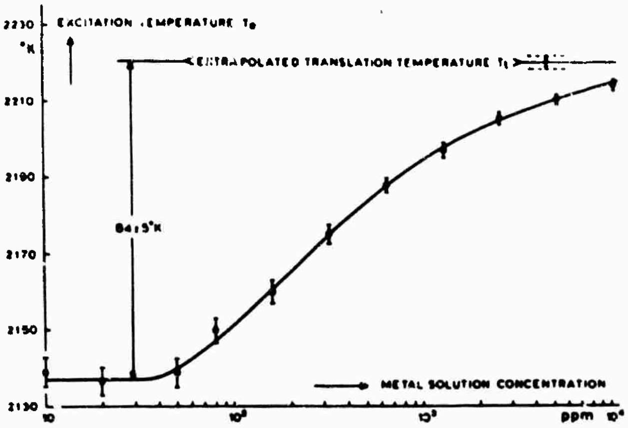

FIG. 7. Excitation temperature T_e, measured by Na line-reversal, is plotted versus Na solution concentration in a $H_2/O_2/Ar$ flame. The symbol ΔT_L represents the deviation of T_e from the true (translational) temperature T_t in the limiting case of low metal concentrations, as found from the high density values of T_e.
(Courtesy of Dr. H. Hooymayers).

The extrapolated translational temperature T_t can be found by making use of the relation $\Delta T = CN_0^{-\frac{1}{2}}$ at three different high metal concentrations C_1, C_2 and C_3, according to

$$\frac{T_e(C_2) - T_e(C_1)}{T_e(C_3) - T_e(C_2)} = \frac{\{C_2/C_1\}^{\frac{1}{2}} - 1}{1 - \{C_2/C_3\}^{\frac{1}{2}}} \qquad (13)$$

From Fig. 7 we find $\Delta T_L = 84 \pm 5$°K. The p-value of this flame is known: $p = 0.32$. From this value we may calculate (cf. Eq.11): $\Delta T_L = 80 \pm 3$°K, in very good agreement with the above experimental result.

Conversely the p-factor can be found from the rise in excitation temperature with increasing metal concentration, provide that p is not too small(17).

When plotting ΔT double logarithmically as a function of the metal solution concentration we may check the behavior of ΔT at high concentration (See Fig. 8).

From the figure we conclude that with high solution concentration ΔT varies as $(N_0)^{-\frac{1}{2}}$ as predicted by theory for a Lorentzian line shape.

V. Departures From Saha Ionization Equilibrium of Metal Vapor in the Flame

The measurements discussed here have been performed with alkali metals in $CO/O_2/N_2$ and $CO/O_2/Ar$ flames. In these flames the following assumptions were experimentally confirmed:(5,6)

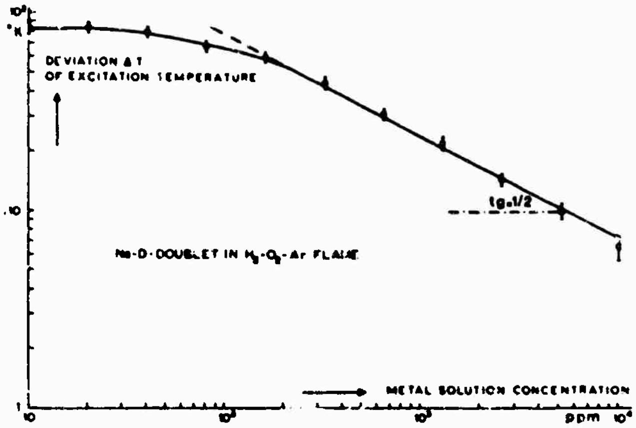

FIG. 8. Double logarithmic plot of ΔT versus Na-solution concentration
(Courtesy of Dr. H. Hooymayers).

(i) No electrons or ions are present in the metal-free flame.
(ii) The Na line-reversal temperature describes adequately the partition of energy over all degrees of freedom relevant in the ionization and recombination processes.
(iii) The temperature at each height is constant over the cross-section of the central flame part
(iv) The total alkali content is constant as a function of height in the central part of the flame.
(v) No alkali molecules are formed in the flame.

Let us consider a monovalent metal M at temperature T. The over-all reactions leading to ionization and recombination of M, respectively, may be represented by:

$$M \underset{s}{\overset{m}{\rightleftarrows}} M^+ + e \qquad (XI)$$

Here m and s represent the rate constants of the ionization and recombination reactions, respectively. Equilibrium is established, if $mM = sM^+ \cdot e$, i.e., if the Saha Equation is valid, with $m/s = I(T)$.

The colored central part in these flames may be approximated as a homogeneous one-dimensional flow system under steady-state conditions. When ambipolar diffusion is neglected (which neglect is experimentally justified(5,6)), the following equation connects the concentrations of metal atoms, ions and electrons

$$q = s(M^+)^2 + v \frac{dM^+}{dx} \qquad (14)$$

where q = reaction rate of ion formation (in cm^{-3} sec^{-1}); s = rate constant of recombination (in cm^3 sec^{-1}); M^+ = concentration of ions (in cm^{-3}) and x = vertical distance from the reaction zone (in cm).

From this Eq. we may derive an equation for the atomic content, M, by converting the flame height scale (x), into a time scale (t) according to $x = v \cdot t$ and by substituting $\bar{M} = M + M^+$, where $\bar{M} = M + M^+$ and $q = mM$

$$-\frac{dM}{dt} = mM - s(\bar{M} - M)^2 \qquad (15)$$

This Eq. will be used to describe the behavior of M versus t, while allowance is made for the variation of m and s with T and with t.

If all degrees of freedom in the flame, that are relevant in the ionization and recombination process, are equilibrated at the local temperature T, then m and s are related by

$$m_{th}(T) = s_{th}(T)\, I(T) \qquad (16)$$

where I(T) is the ionization constant, and m_{th} and s_{th} represent the rate constants under the equilibrium conditions mentioned.

If these equilibration conditions were locally fulfilled throughout the flame and if m and s were infinitely large, then the fraction of ionized metal would correspond to Saha-equilibrium at any locus of the flame at the prevailing temperature.

From Eqs. (15) and (16) we find

$$-\frac{dM}{dt} = m_{th}\left\{M - \frac{(\bar{M} - M)^2}{I(T)}\right\} \qquad (17)$$

When determining photometrically the variation in atomic metal content with height ($\propto$ rise-time) for a certain total metal content $\bar{M}$ in the flame, we are able to compare this behavior with the variation predicted by the Saha Law (at varying temperature). Both curves are plotted in the next figure for three alkali metals.

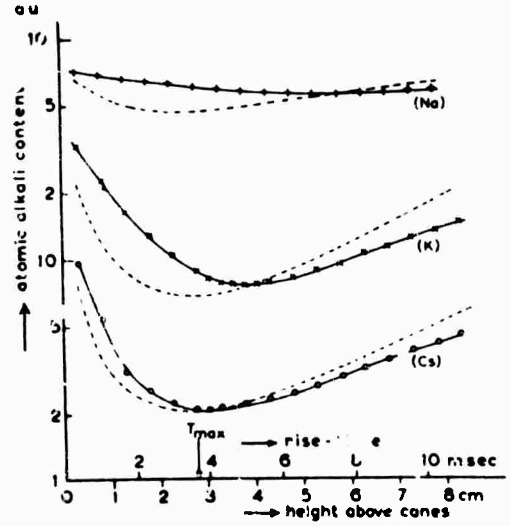

FIG. 9. The measured atomic metal content as a function of height above the blue cones in a CO-flame (T_{max} ~ 2500°K). The dotted curves represent the corresponding Saha curves.

In the construction of these "theoretic Saha-curves" we used the fact that they should virtually intersect the corresponding experimental curves at the point where the latter attain their minimum value, i.e., where $\frac{dM}{dx} = 0$ (and thus $\frac{dM}{dt} = 0$). This holds because for vanishing value of the left-hand side of Eq. (17) this equation becomes identical to the Saha-equation. Furthermore, in this construction, one needs either the absolute value of $\bar{M}$ or the ratic $M/\bar{M}$ (in any point of the experimental curve) for the metal solution sprayed. The absolute value of $\bar{M}$ is found from self-absorption measurements(5-8), that of $M/\bar{M}$ is based on ionization suppression measurements in the minimum point of the experimental curve(5,6).

From Fig. 9 one sees that there is a time lag in the establishment of Saha equilibrium, as, roughly speaking, the experimental curves are displaced with respect to the theoretical Saha curves over a time-interval of the order of 1 msec. One may conclude that the rate constants are indeed not infinitely large compared to the time scale considered and/or that the flame gases are not fully equilibrated as far as the reactions leading to ionization or recombination are concerned.

Let us suppose that well above the point of maximum temperature the flame gases are in thermal equilibrium. Then the behavior of the atomic content M is given by Eq. (17). This equation may be easily transformed into:

$$-\frac{d\ln M}{dt} = m_{th}\left\{1 - \frac{(\bar{M} - M)^2}{MI(T)}\right\} \qquad (18)$$

From the experimental M-curve, from the known absolute value of $\bar{M}$ and the measured temperature profile one calculates m_{th} from this equation(5,6). The results obtained downstream the temperature maximum for several $CO/O_2/N_2$ flames, covering a temperature range from 2200 to 2500°K, are plotted in the next figure for Na, K and Cs as a function of the reversal temperature at the point where m_{th} was determined.

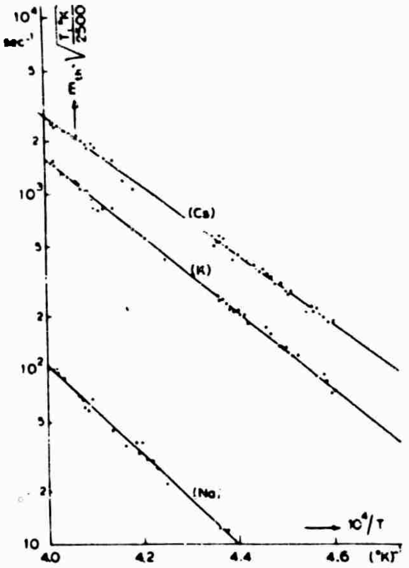

FIG. 10. The values of m_{th} as a function of T^{-1} are presented. The solid (semilogarithmic) straight lines represent the functions C exp $(-E_i/kT)$ with E_i = ionization energy of Na, K and Cs respectively.

The m_{th} values plotted are not corrected for the contribution of thermal chemi-ionization, but this contribution is at most 4-8% in these flames and may thus be disregarded. Corrections were made for the variations of collision frequency and number of flame gas molecules with temperature (See below). The m_{th}-plot appears to be a straight line, the slope of which fairly well corresponds to the ionization energy, E_i, of the metal considered divided by the Boltzmann constant, K.

For the interpretation of the dependence of m_{th} on T it is useful to express the mechanism of ionization in terms of collision processes. In close agreement with mechanisms found for metal excitation and quenching processes (See above) we assume that ionization mainly results from a transfer of internal (vibrational and/or rotational) energy of the colliding flame molecules to the atom to be ionized. We then may formally write

$$m_{th} \propto \sqrt{\frac{T}{\mu}} \cdot N \cdot Q_{ion}\, \exp(-E_i/\quad) \qquad (19)$$

where μ = reduced mass, Q_{ion} = ionization cross-section and N is total number of flame gas molecules.

Since a flame contains molecules of various kinds μ and Q_{ion} refer to some sort of average value. In our flames N_2, CO_2 and CO are the most important constituents. Assuming in first approximation that the $Q_{ion}^{(j)}$ - values vary with the gas-kinetic diameter of the molecules and knowing the quantitative composition of the burnt gases, we may calculate the variation of the average value $Q_{ion}/\sqrt{\mu}$ in the different flames. This variation appeared to be at most 1, 2 and 4% for Na, K and Cs, respectively, so we may neglect this variation in the flames considered.

N varies as T^{-1} for flames at atmospheric pressure, so it follows that $m_{th}\sqrt{T(^{\circ}K)/2500}$ as plotted in fig. 10, should vary with temperature according to $\exp(-E_i/KT)$. Since the actual temperature dependence found is fairly well described by this function, we may afterwards conclude that Q_{ion}/μ is virtually independent of temperature in the range investigated, and that the (internal) energy distribution of the relevant molecules is in thermal equilibrium.

Recent measurements of Jensen and Padley(39), on the ionization of alkali metals in $H_2/O_2/N_2$ flames support very nicely the behavior of m_{th} as a function of T^{-1} found in our measurements. They concluded from their results that all bulk flame gas molecules are approximately equally efficient in causing alkali metals to ionize in full agreement with our observations. Furthermore, they point out that the first preliminary observation on the activation energy for ionization of sodium in H_2-flames(40), which suggested an activation energy of about $\frac{1}{2}E_i$, is most probably in error. So this contradictory observation seems to be settled.

Recent measurements by Kalff and Thomeer(41) on the ionization of strontium in (dry and moist) CO-flames with temperatures in the range from 2400 to 2600°K proved that the activation energy involved equals the ionization energy within ± 5%.

From fig. 10 one may conclude that the relaxation effect for a given metal increases with decreasing ionization rate, i.e. at decreasing temperature. The larger the ionization energy of the metal the more pronounced the relaxation effect is.

The dependence of the over-all cross section for ionization Q_{ion}, on the qualitative flame gas composition was further investigated by replacing N_2 by Ar in the flame. Argon having no internal degrees of freedom is expected to have low ionization efficiency (as it has in excitation and deactivation of metal levels. (See above).

The result showed that the m_{th}-values for K and Cs in a temperature range from 2230 to 2330°K, varied with temperature according to $\exp(-E_i/KT)$. In particular we found that the m_{th}-values decreased by about 61% upon replacing N_2 by Ar (at the same temperature, T = 2300°K), whereas the decrease of the partial pressure of all flame molecules together was about 57%. (After correction for the variation in averaged reduced mass, this difference became still somewhat smaller)(6) These outcomes support strongly our concept that the transfer of internal energy during collisions between gas molecules and alkali atoms is the most likely mechanism for metal ionization in the flame.

We propose the following reaction mechanism

$$M + X^* \underset{m}{\overset{s}{\rightleftharpoons}} M^+ + e + X \qquad \text{(XII)}$$

where X is flame molecule. This mechanism is proposed by other authors too(20,40,42,2,43,39). Other ionization mechanisms that are suggested are

$$M + OH \rightleftharpoons M^+ + OH^- \qquad \text{(XIII)(cf.lit.(44)}$$

$$M + e^- \rightleftharpoons M^+ + 2e^- \qquad \text{(XIV)(cf.lit.(44)}$$

and $$M + H_2O \rightleftharpoons MH_2O^+ + e^- \qquad \text{(XV)(cf.lit.(45)}$$

Reactions (XIII) and (XV) can hardly play a part in our CO-flames because of low OH- and H_2O-contents. Besides Jensen and Padley have proved(39) that reactions (XIII) and (XIV) can both be rejected in the H_2-flames, since the ionization takes place through a process which is first order with respect to free atomic metal and which is pseudo first-order overall in a given flame. Reaction (XV) can be ruled out because of the experimental outcome that the activation energy found corresponds very well to the ionization energy of the metal involved (cf.lit.(39).

For simplification we assume the flame consists of N_2-molecules at constant temperature, T, throughout the subvolume considered. The energies available (vibrational, rotational, translational and excitation energy) are supposed to be distributed according to the Boltzmann formula. The discrete vibrational energy levels of the molecules are approximately equidistant ($h\nu_0 \sim KT$). In our picture small amounts of rotational and kinetic energy may be transferred simultaneously during the collision and thus supplement the vibrational energy transferred. Then the vibrational energy E_v transferred may be considered as if it was distributed continuously. The atom to be ionized possesses a virtually infinite number of electronic excitation levels with energy E_j. In principle the occupation of these levels obeys the Maxwell Boltzmann Law. For simplification we suppose that Q_{ion} is constant for any value of j and is independent of the excited state of the molecule and of the kind of energy transferred. This Q_{ion} refers to some sort of average value. Under the assumption that ionization of the atom occurs if $E_j + E_v \geq E_i$ we find for m_{th}(5,6,46)

$$m_{th} = NQ_{ion}\left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}} \exp(-E_i/\ T) \sum_{j=0}^{\infty}\left\{\frac{g_j}{Z}\right\} \qquad (20)$$

where Z is the (electronic) partition function of the atom and g_j is the statistical weight factor of the j^{th} excitation level of the atom.

In this equation the infinite summation $\sum_{j=0}^{\infty} g_j$ occurs. In order to circumvent this difficulty we split this summation in two parts: one summation over the excitation levels with $E_j \leq E_i - kT$ $(0 \leq j \leq n)$ and the other over the remaining energy levels. Assuming that the Boltzmann distribution is still valid for the levels with $j \leq n$, we can evaluate the first summation and we are able to derive Q_{ion}-values from the m_{th}-values experimentally found (according to Eq. (20)). It should be noted that if we had chosen E_n smaller or larger by $\frac{1}{2}kT$, the Q_{ion}-values would be raised and lowered, respectively, by factors of about 2.5 and 3.0.

As regards the second term of the above summation one may remark the following: When the atom is in an excited state with energy E_j $(j > n)$, which approaches the ionization energy E_i within kT, we may assume that each collision with a flame molecule leads to ionization. The summation over the energy levels with $J > n$ leads to a finite value(6). Yet it should be noted that for energy states in the environment of the ionization state, several complications may be expected: the general Boltzmann distribution of the excitation energies might no longer be valid; the highly excited atoms have diameters that compare with interatomic distance. If the ionization process is not equilibrated, there will be no equilibrium with respect to the occupation of the higher electronic levels, which may be fed for a noticeable part by ion-recombination. The implications and consequences of the above deviations are still under investigation.

From the experimental m_{th}-values at T = 2500°K we calculate now the following (under-limiting) values of Q_{ion}:

$Q_{ion}(Na) = \pi \cdot 69$ Å^2, $Q_{ion}(K) = \pi \cdot 29$ Å^2 and
$Q_{ion}(Cs) = \pi \cdot 9$ Å^2

The order of magnitude of these values compare fairly well to that of gas-kinetic cross-sections being in the order of (30-80) Å^2 and to the quenching cross-sections (cf. Sec. IV) amounting to (10-100) Å^2.

It should be noted that the Q_{ion}-values increase in the sequence Cs - K - Na, whereas the corresponding gas-kinetic cross-sections decrease in this sequence. Most probably some efficiency factor has still to be taken into account, when comparing Q_{ion}-values with gas-kinetic cross-sections. We have only considered N_2-molecules. The Q_{ion}-values found from our experiments refer to a kind of average values as regards the kind and the excitation states of the molecules and the atom.

Our m_{th}-values for Na, K and Cs at 2250°K amounting to 9.0, 190 and 400 sec^{-1}, respectively, may be compared with those obtained by Jensen and Padley(39). They found the following values: 7.2, 280 and 4000 sec^{-1}, respectively, for Na, K and Cs. We have no explanation for the discrepancy in the case of Cs.

For comparison we give the result for m_{th}(Sr) in the CO-O_2-N_2 flames(41); for temperatures ranging from 2400 to 2600°K the m_{th}(Sr) varied from 1.9 to 11.8 sec^{-1}. Herefrom we derive a Q_{ion}(Sr) value of about π x 120 Å^2. (at T = 2500°K), comparable to the values found for Na, etc.

From the m_{th}-values the corresponding values of the recombination rate constant s_{th} may be derived according to Eq. (16). We compare our values with those found in the literature.

In the below comparison we must note that the values in lit.(43) refer to metal solutions sprayed ranging from 0.01-0.1 N. The s-values found depend on the kind of salt used and on the metal content in the flame. We investigated the latter dependence by measuring m_{th} (and s_{th}), for Na, K and Cs for metal concentrations varied by a factor of eight and found no dependence of m_{th} (and s_{th}) on the metal content. This outcome should be expected if the ionization proceeds as suggested in our work.

At a given temperature the s_{th}-values found by us decrease in the sequence Na-K-Cs, i.e. with decreasing ionization potential. This holds throughout the temperature range considered. This result is in agreement with the results of King(43) and those of Knewstub and Sugden(47). The results of Jensen and Padley(39) are consistent with our results. It should be noted that the s_{th}-value of Sr(41) appeared to be larger than that of Na. Since Sr has also a larger ionization energy, this outcome seems to fit in the picture above.

Finally we consider the ionization and recombination processes in the flame region downstream the temperature maximum. In this region the m-values found appear to exceed the m_{th}-values as derived from fig. 10 for comparable temperatures. For an explanation we suggest chemi-ionization reactions caused by three-body collisions involving CO and excess O (cf. the chemiluminescent reaction (III)). (Reactions involving excess H and OH do not play a part because of the low partial pressures of H and OH in the CO-flames). This non-thermal chemi-ionization proceeds then according to

$$CO + O + M \rightarrow CO_2 + M^+ + e \qquad \text{(XVI)}$$

The probability of this reaction may be enhanced by considering this reaction to be composed of two successive steps $CO + O + X \rightarrow CO_2 + X^*$ (where X is flame molecule) followed by: $X^* + M \rightarrow X + M^+ + e$ Similar two-step processes have been discussed elsewhere(2,6,15,17) in connection with the suprathermal excitation of alkali atoms. It should further be noted that Wigner's Rule is obeyed in reaction (XVI) when M is an alkali metal(6)

We may formally write for the m- and s- values actually found: $m = m_{th} + m_{exc}$ and $s = s_{th} + s_{exc}$. It is now assumed that

$$m_{exc} \propto \left\{[CO][O] - [CO]_{eq}[O]_{eq}\right\} \qquad (21)$$

and likewise:

$$s_{exc} \propto \left\{[CO_2] - [CO_2]_{eq}\right\} \qquad (22)$$

Since $[CO_2] \sim [CO_2]_{eq}$ (cf. Sec. III), we may neglect s_{exc}(5,6). From Eq. (15) we now derive:

$$m_{exc} = \frac{1}{M}\left\{\frac{m_{th}}{I(T)}\,(\bar{M} - M)^2 - \frac{dM}{dt}\right\} - m_{th} \qquad (23)$$

From this equation the values of m_{exc} can be calculated, since all quantities involved are known (cf. figs. (9) and (10)).

The actual O-content in the flame can now be derived from the temperature profile in the flame and $[CO] \sim [CO]_{eq}$ (cf. Sec. IIIa). $[O]_{eq}$ and $[CO]_{eq}$ can be calculated in each point of the flame when the supply of fuel and oxidant gasses and local temperature are known (cf. Sec. II).

When plotting the m_{exc}-values experimentally found for K and Cs as a function of $\{[CO][O] - [CO]_{eq}[O]_{eq}\}$ we find in good approximation a straight line through the origin(6). This is a nice experimental confirmation for the chemi-ionization

TABLE 2. COMPARISON OF EXPERIMENTAL s_{th}-VALUES (I CM^3 SEC^{-1}) WITH LITERATURE DATA

Salts Sprayed	Air-C_3H_8 Flame* T = 1970°K (43)	H_2/O_2 Flame T = 2400°K (47)	Air-C_2H_2 Flame T = 2500°K (1)	H_2/O_2-Flame T = 2400°K (48)	CO/O_2/N_2-Flame T = 2400°K (5,6)
LiCl	(6.5 - 9.0) x 10^{-9}	---	---	---	---
Li_2CO_3	(7.8 - 9.2) x 10^{-9}	5 x 10^{-9}	---	---	---
NaCl	(1.9 - 2.8) x 10^{-9}	---	---	---	8.7 x 10^{-9}
Na_2CO_3	(3.1 - 4.0) x 10^{-9}	4 x 10^{-9}	---	---	---
KCl	(0.18 - 0.25) x 10^{-9}	---	> 3.0 x 10^{-9}	3.3 x 10^{-9}	3.2 x 10^{-9}
CsCl	(0.17 - 0.25) x 10^{-9}	---	---	---	0.68 x 10^{-9}

* for metal concentrations in the range 0.01 - 0.1 N

mechanism proposed.

From the slope of both curves the following rate constants could be derived:

$$k_{16}^{K} = 7 \times 10^{-32}\ \mathrm{cm}^{6}\ \mathrm{sec}^{-1} \text{ and } k_{16}^{Cs} = 1.4 \times 10^{-31}\ \mathrm{cm}^{6}\ \mathrm{sec}^{-1}$$

Using the above rate constant values we are able to derive the contribution of thermal chemi-ionization to the m_{th}-value. These calculations showed that this contribution was negligibly small as compared to the thermal ionization due to collisions with flame gas molecules (See above).

VI. Mechanisms of Alkaline-Earth Oxide Dissociation in CO-Flames

In hydrogen containing flames the formation and dissociation of alkaline-earth oxides proceeds most probably by the following reactions, where M is a metal atom(49)

$$M + H_2O \rightleftharpoons MO + H_2 \qquad \text{(XVII)}$$

and/or

$$M + OH \rightleftharpoons MO + H \qquad \text{(XVIII)}$$

Taking into account the change in enthalpy of reactions (XVII) and (XVIII) for Ca, Sr and Ba, it is reasonable to assume that in flames at atmospheric pressure these binary reactions are sufficiently rapid to be balanced at any point above the reaction zone. (In ordinary flames, the concentration of particles occurring in reaction (XVIII) may be of an order of magnitude less than those occurring in reaction (XVII)).

Deviations of the radical concentrations from their equilibrium values will not affect the degree of dissociation of the alkaline-earth oxides, as long as the concentrations of the stable major species H_2 and H_2O are not affected by these deviations. This holds also if reaction (XVIII) were the prevailing one, because of the rapid, equilibrated exchange reaction $H + H_2O \rightleftharpoons OH + H_2$ (See Sec. (III)).

Since the greater part of the alkaline-earth metal is present in the flame as oxid(6,7,50), the atomic metal content is not expected to be directly affected by radical deviations. This holds not a priori for the metal hydroxides.

In dry CO-flames the above reactions are not expected to be effective. In these flames the concentrations of H-compounds is suppressed to a negligible amount(6,7)

We have determined photometrically in these flames (with temperatures ranging from 2200 to 2550°K) dissociation energies of Ca-, Sr- and Ba-oxides in two independent ways based on the assumption that the state of dissociation corresponds to equilibrium at the measured temperature(6,7). Consistent results were obtained when

(i) the height of observation above the reaction zone was varied from 0.8 to 4.5 cm

(ii) the flame temperature (and flame gas composition) was varied

(iii) the moisture of the flame was varied by supplying additional water vapor.

The results compare satisfactorily with other recent data from flame photometric work in the literature(7,51-54). This implies that in our dry CO-flames an equilibrium dissociation of the metal oxides is established at a sufficiently rapid rate. The observation that ionization does not upset the oxide to metal ratio in the flame may be considered as a further argument for a rapid equilibration of the dissociation reaction(6,7,55). We want to discuss the reactions that may explain this outcome:

The direct dissociation and recombination reaction

$$MO + X \rightleftharpoons M + O + X \qquad \text{(XIX)}$$

would require a third body X. It seems highly improbable, using gas-kinetic cross-section data, that sufficient dissociating collisions will have occurred for the establishment of an equilibrium state, when the flame gases have traveled away from the reaction zone over a distance of about 1 cm corresponding to a rise-time of 1 - 2 msec Step-up processes involving intermediate (vibrationally) excited states of the oxide molecule, might enhance considerably the over-all probability of a dissociating collision (cf. similar mechanism for explanation of large ionization cross-sections in Sec. V).

But, even if reaction (XIX) should be sufficiently rapid, it must be ruled out, as the main dissociation reaction, since it would make the degree of dissociation explicitly dependent on the atomic oxygen content. This content is known (See Secs. III and V) to exceed its equilibrium value markedly, especially so directly above the cones. This excess O-content depends on temperature, fuel-to-oxidant ratio, etc. In our CO-flames this excess factor of O-content may be as high as two to eight(6,7). This would have introduced a systematic error of 3 to 9 kcal/mol in our determination of dissociation energies. Since our results under varying conditions were mutually consistent within an accidental error of 2.5 kcal/mol(6,7) we have to reject reaction (XIX).

We believe that the consistency of our experimental dissociation energy values can be explained, in analogy with reaction (XVII), by the rapid equilibrated reaction

$$MO + CO \rightleftharpoons M + CO_2 \qquad \text{(XX)}$$

CO- and CO_2 contents virtually equal their equilibrium values, regardless of the deviation in atomic O-content(15) (See also Secs. III and V). The change in enthalpy amounts to 24, -16 and -1 kcal/mol for Ca, Sr and Ba, respectively. This reaction parallels the well-known water-gas equilibrium reaction

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \qquad \text{(XXI)}$$

which links up reaction (XXI) with (XVII) in hydrocarbon flames. (Therefore it is hardly possible to discriminate between these reactions in these flames)

However, the spin-conservation rule seems not to be satisfied in reaction (XXI), CO and CO_2 having singlet electronic ground states. A similar difficulty exists in the combustion reaction $CO + O \rightarrow CO_2$ (See Sec. III), which is still believed to be possible, however. Possibly the formation of alkaline-earth atoms in an excited triplet state through reaction (XXI) should be considered. In this case the change in enthalpy amounts to +20, +26 and +25 for Ca, Sr and Ba, respectively. We may remark that Wigner's rule is obeyed also in reaction (XVIII) only if metastable metal states are considered. Another possibility is the formation of CO_2 molecules in an excited $^3\Pi$ state.(55)

VII. Excitation Energies of Some Visible Alkaline-Earth Bands

When alkaline-earth salts are introduced into a flame or arc strong emission bands are observed in the visible spectral region. They have usually been attributed to the oxides, but their complex structure has not yet been resolved in detail. The correct assignment and analysis of the alkaline-earth band spectra is of interest for various reasons. The systems of CaO, SrO and BaO that have been analyzed seem to involve a $^1\Sigma$ state of the lower level(56-58). This singlet state possibly not correlates upon dissociation with ground state atoms $M(^1S) + O(^3P)$ because of Wigner's rule. (cf. also Sec. VI). Another possibility is that the singlet ground state of the MO-molecules dissociates into a pair of atoms, one or both of which are in an excited triplet state. Birge-Sponer extrapolation method based on the vibrational analysis of the bands gives quite too low values of the CaO and SrO dissociation energies(59-61). This result may suggest that the actual ground state which differs from the lower excited level involved in the band emission might be an unknown triplet level.

Measurements of Huldt and Lagerqvist(60,62) have shown that the $^1\Sigma$ terms in CaO and SrO are not to be identified with the ground state.

There are indications in the literature that other stable molecular compounds such as MOH, M_2O, MO_2, M_2 and $M(OH)_2$ might be present in the flame. It is suggested that MOH molecules are responsible for the visible alkaline-earth bands.(63,64,66,67) Strong evidence for the occurrence of MOH in H_2-containing flames has been obtained from photometric flame measurements(68-71). A recent publication of Sugden and Schofield(72) suggested that $(MOH)_2$ might be much more important than (MOH) in $H_2/O_2/N_2$-flames.

Our spectrographic observations of the alkaline-earth spectra in dry and moist $CO/O_2/N_2$-flames, $C_2H_2/O_2/N_2$- and $C_3H_8/O_2/N_2$-flames(6,50) led to the conclusion that the visible band spectra should be attributed mainly to MO molecules. In order to produce additional evidence for this outcome we measured the excitation energy for some visible bands of CaO, SrO and BaO in CO-, H_2- and C_2H_2-flames.

The absolute value of the excitation energy of a molecular band, $E_{MO}^{(1)}$, can be determined as follows: The difference of the $E_{MO}^{(1)}$-values of two bands (measured at the band heads) of the same alkaline-earth molecule can be found from the equation. (This difference is independent of O-content and dissociation energy).

$$E_{MO}^{(2)} - E_{MO}^{(1)} = k\left\{\frac{1}{T_1} - \frac{1}{T_2}\right\}^{-1} \ln\left\{\left(\frac{u_{MO}^{(1)}}{u_{MO}^{(2)}}\right)_{T_1}\left(\frac{u_{MO}^{(2)}}{u_{MO}^{(1)}}\right)_{T_2}\right\} \quad (24)$$

where T_1 and T_2 are two (different) flame temperatures and $u_{MO\,T_1}^{(1)}$, etc. represent the band intensities (apart from a constant) for the two bands, respectively, at temperatures T_1 and T_2.

The absolute value of $E_{MO}^{(1)}$ can be determined following the method applied by Huldt and Lagerqvist(62,60). The band emission (corrected for ionization) is measured as a function of flame temperature, with a given metal solution sprayed. The corresponding meter defection, u_{MO}, satisfies the following relation

$$u_{MO} \propto [MO] \cdot l \cdot \exp(-E_{MO}/kT) \quad (25)$$

where l is the thickness of the colored flame part, [MO] the concentration of molecules MO, and E_{MO} the excitation energy.

By plotting $\ln(u_{MO})$ versus $(kT)^{-1}$ (after correcting for the possible change in l and [MO] with varying temperature) we find E_{MO} for the band considered from the slope of the curve. In order to correct for the variations in l and [MO] upon variations in temperature, we measured the corresponding variations in the ~~Na-D-~~ doublet emission. Herefrom we derived after correcting for the varying temperature, the relative change in the product $l\bar{N}$ ($\bar{N}$ refers to the total element concentration in cm^{-3} present in the flame part investigated). It should be remarked that not only $\bar{N} = [MO] + [M]$ may vary, but also the ratio $[MO]/[M]$. The variations in [MO] due to a shift in dissociation equilibrium with varying temperature can be derived from the calculated oxygen content in the flame at the different temperatures, and from the (known) dissociation energy.

In the measurements outlined above some assumptions have to be made and experimentally confirmed

(i) The population of the excited states involved in the band emission must obey the Maxwell-Boltzmann formula at the relevant temperatures, i.e. thermal equilibrium should exist (cf. Sec. I).

(ii) The actual oxygen concentration is supposed to be equal to the equilibrium concentration.

(iii) The molecular species responsible for the band emission observed is ascribed to oxide molecules only. (We will show later in this section as to what extent this assumption holds in our flames.)

The flame temperature was varied in two different ways: by adding additional amounts of nitrogen the temperature in the flame can be lowered by 200-300°K; the temperature can also be varied by observing different heights in the flame. In the latter case we could obtain temperature variations in the order of 200°K, especially in lean flames.

In order to meet assumptions (i) and (ii) the height in the flame was varied in the region upstream the temperature maximum. In this region thermal emission prevails and the oxygen content equals there the equilibrium value (cf. Sec. III).

Some results in the $CO/O_2/N_2$-flame are given in Fig. 11.

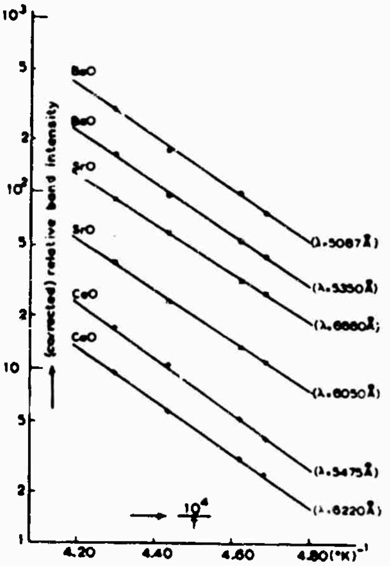

FIG. 11. Semi-logarithmic plot of the intensity of some bands of Ca, Sr and Ba against the reciprocal temperature.

From the straight lines in Fig. 11 we may conclude that the population of the excited states involved is thermal indeed. The E_{MO}-values derived from this graph are given below (See Table 3). It should be noted that the E_{MO}-values found were used for the derivation of dissociation energies, D_{MO}, of the alkaline-earth oxides from line/band ratios. Since these D_{MO}-values appeared to agree very well with the D_{MO}-values derived in an independent method(6,7), the E_{MO}-values are reliable ones. Furthermore their differences are in good agreement with the energy differences found independently according to Eq. (24) (See Table 4). Since in our CO-flames only MO-molecules are present, we may be certain that our E_{MO}-values refer to excitation energies of alkaline-earth oxide bands.

The same measurements were repeated in H_2- and C_2H_2-flames, with temperatures ranging from 2250 to 2500°K (73). No correction was made for the formation of MOH and/or $M(OH)_2$-molecules. The semi-logarithmic plots are again straight lines, i.e. the populations involved are fairly thermal. The results are given in the next table, in comparison with some literature data.

From the data given in Tables (3) and (4) we may conclude:

(i) The same emitters, i.e. oxide molecules are most likely responsible for the visible alkaline-earth band emission in CO-, H_2- and C_2H_2-flames, since the E_{MO}-values in the three flames agree very well.

(ii) No evidence was found for the formation of MOH and $M(OH)_2$-molecules in the three kinds of flames investigated (See above)

(iii) The results found indicate that the lower level involved in the visible band emission does not coincide with the molecular ground state (cf. also lit. (60) and (62)).† (The latter was found to be a $^3\Pi$ state rather than a $^1\Sigma$-state(6,7).

The experimental results obtained from photometric measurements confirm nicely our previous spectrographic results(6). (See also above).

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TABLE 3. EXCITATION ENERGIES OF ALKALINE-EARTH BANDS (IN eV)

Metal	Wavelength of Band Head (Å)	E_{MO} in C_2H_2-Flame*	E_{MO} in H_2-Flame**	E_{MO} in CO-Flame +	E_{MO} in C_2H_2-Flame++	E_{MO} in H_2-Flame++
Ca	5475	4.47 ± 0.28	4.96 ± 0.30	3.14 ± 0.04	3.21 ± 0.10	3.14 ± 0.05
	6020	---	--	---	3.30 ± 0.10	3.18 ± 0.05
	6220	3.97 ± 0.24	4.72 ± 0.28	2.99 ± 0.03	3.02 ± 0.10	2.98 ± 0.05
Sr	6060	3.47 ± 0.22	3.60 ± 0.23	2.89 ± 0.03	3.04 ± 0.10	2.9[illegible] ± 0.05
	6450	---	---	---	2.92 ± 0.10	2.95 ± 0.05
	6660	3.35 ± 0.20	3.47 ± 0.22	2.80 ± 0.03	2.93 ± 0.10	2.76 ± 0.05
	6820	---	---	---	3.04 ± 0.10	2.90 ± 0.05
Ba	4873	---	---	---	---	3.28 ± 0.05
	5087	---	---	2.96 ± 0.05	---	2.98 ± 0.05
	5230	---	---	---	---	3.17 ± 0.05
	5350	---	---	3.43 ± 0.15	---	3.38 ± 0.05

* cf. lit. (62)
** cf. lit. (60)
\+ cf. lit. (6,7)
\++ cf. lit. (73)

TABLE 4. DIFFERENCES IN EXCITATION ENERGY (IN eV) FOR THE ALKALINE-EARTH BAND MEASURED INDEPENDENTLY (ACCORDING TO EQ. (24))

Metal	Band Heads in Å	CO-Flame	C_2H_2-Flame	H_2-Flame
Ca	$E_{5475} - E_{6020}$	---	-0.12 ± 0.05	-0.14 ± 0.05
	$E_{5475} - E_{6220}$	0.22 ± 0.03	0.14 ± 0.07	0.13 ± 0.05
Sr q	$E_{6060} - E_{6450}$	---	0.15 ± 0.05	0.02 ± 0.04
	$E_{6060} - E_{6660}$	0.13 ± 0.03	0.12 ± 0.04	0.13 ± 0.03
	$E_{6060} - E_{6820}$	---	0.07 ± 0.05	0.18 ± 0.04
Ba	$E_{5350} - E_{4873}$	---	-0.49 ± 0.10	-0.35 ± 0.10
	$E_{5350} - E_{5087}$	0.47 ± 0.04	0.52 ± 0.05	0.46 ± 0.08
	$E_{5350} - E_{5230}$	---	-0.06 ± 0.03	-0.10 ± 0.03

---

† Recently Capacho-Delgado and Sprague have observed absorption of the green Ba resonance line in the 5475Å band system of Ca(74). This observation indicates that possibly this green Ca band system involves a transition to the molecular ground state, and is consequently inconsistent with the results given in Table 3.

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