TECHNICAL REPORT # 22
TO
ADVANCED RESEARCH PROJECTS AGENCY

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

Principal Investigator: H. P. Broida

University of California
Santa Barbara
Physics Department

July 1, 1967

Reproduction In Whole Or In Part Is Permitted
For Any Purpose Of the United States Government
BEST
AVAILABLE COPY
PHOTOMETRIC MEASUREMENTS ON THE DEVIATIONS FROM THE EQUILIBRIUM STATE IN BURNT FLAME GASES
Tj. Hollander
Department of Physics, University of California
Santa Barbara, California

Abstract

Photometric investigations are reported in laminar, premixed shielded flames above the reaction zone, burning at atmospheric pressure. In these CO/H₂/O₃, C₆H₆/H₂/O₂, and H₂/O₃ 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 the flame gas mixture approaches what extent 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 distribution 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 equilibria appear 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.

(1) generally the temperature is locally different from the equilibrium value
(2) at a given locus in the flame the energy may not be distributed among one another

Ad (1): 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 CO₂₃, H₂O, N, 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 recombin slow to stable molecules and consequently the flame gas mixture approaches gradually to a complete chemical equilibrium state.

I. Introduction

a. Object of our Study

In this paper some deviations from the equilibrium state are discussed. They occur in 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/CO₂/H₂/O₂ and CO₂/H₂/O₂ flames (sometimes H₂ is used instead of CO₂ or N₂, or both) 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 spray 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.

b. Equilibrium

Before discussing deviations from the equilibrium state we first define general thermodynamic
Because of the energy released in the radical recombination 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 equilibrated 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 (iii) 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 to the 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 sec with the surrounding molecules, (6,26). The flame gases cover a distance of 5-15 mm from the reaction zone upwards in 1 sec. 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, (6,26,29). The equilibration of the vibrational degrees of freedom proceeds more slowly. A serious lag in this equilibration is not to be expected in our flames, (2), neither with the higher nor with the lower vibrational levels. 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, (2,6,26).

Concerning the equilibrium ionisation in normally burning, non-sooting, metal-free flames we may refer to the many publications dealing with atomic and electronic species found in and above the reaction zone, (25,5,26). These excess charge 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 ionisation 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 de-population of the higher energy levels of the particles with respect to their lower levels. Only for strong resonance lines ($\pm$ the center of those lines) may we expect that radiation equilibrium exists, at least in the interior part of the flame. The underpopulation of the excited levels depends on the metal concentration in the flame. The flame temperature derived from line-reversal measurements ( = excitation temperature) will consequently be lower than the translational 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 $T$. In the major part of 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 equilibrated (see above) and that there is only one translational temperature (9) (as opposed to the various excitation temperatures). In the following we mean with "temperature" of the flame 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, (9,47). 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 correct for energy losses). 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 part 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 Smelkman, (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:

1. 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 metallic states. When the yield-factor for resonance fluorescense (defined as the fractional possibility that an excited state 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).

Sneileman 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).

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 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 and the specific heats from 296°K to the flame temperature of the final components, and the constants of the dissociative equilibrium 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 dissociation constants and the optical emittance of the gas mixture at 298°K can be calculated from the measured and calculated 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.

* * *

### TABLE I. SEVERAL TEMPERATURES OF VARIOUS SPECTRAL LINES

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength(Å)</th>
<th>Radiation Temp, of Strip Lamp(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>6708</td>
<td>2432 ± 2</td>
</tr>
<tr>
<td>Sodium</td>
<td>5890</td>
<td>435 ± 1</td>
</tr>
<tr>
<td>Potassium</td>
<td>7665</td>
<td>2436 ± 1</td>
</tr>
<tr>
<td>Rubidium</td>
<td>7948</td>
<td>2436 ± 1</td>
</tr>
</tbody>
</table>

### 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(13,20,29). 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 equilibrium. 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, Ja. et Svedberg have given a theoretical treatment of the way in which radical recombination occur, especially in oxygen-lean H₂ / O₃ / N₂(28). Zeegers in our laboratory has made a more general approach and has extended this treatment to CO - and C₂H₂ - flames with different gas composition(12,15). He took also into account: decay of O-radicals thorough the reactions O₀ + O₂ → O₃ and O₀ + O₂ → O₂; variation of the concentrations of H, O, and CO by radical recombination and the production of radicals by thermal dissociation of H₂, H₂O, CO, and O₂, 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:

* * *
Here $N$ is the total number of flame molecules per cm$^3$, $T$ is temperature, namely reactions (III) and (IV). As may be responsible for the initial rise of flame temperature, this is not easily possible.

$H_2 + OH \rightarrow H + H_2O$  
$H_2O + \rightarrow H + OH$  
$O_2 + H \rightarrow O + OH$  
$CO + OH \rightarrow CO + H_2O$  
$CO \rightarrow CO$  
$H + OH \rightarrow H_2 + O$  
$CO + 2H \rightarrow H_2 + CO$  
$CO + 2OH \rightarrow CO_2 + H_2O$  

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

The following partial equilibria are established in our flames for 95% within 10$^{-2}$ 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.

$H_2 + OH \rightarrow H + H_2O$  
$H_2O + \rightarrow H + OH$  
$O_2 + H \rightarrow O + OH$  
$CO + OH \rightarrow CO + H_2O$  

(with equilibrium constants $k_1 \ldots k_6$).

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 proved in detail by Zeegers in our flames reaction (IV) is the predominant one(15). If the temperature rise is not affected by heat losses, the temperature $T_1$, as a function of rise-time, $t$, will reach asymptotically and monotonously its equilibrium value $T_e$. One has

$$\frac{d[H]}{dt} = -k_3[H][CO][O] - k_6[H][CO][O]$$

Taking into account that $k_3[H][CO][O] = k_4[H][CO][O]$, we get

$$\frac{d[H]}{dt} = -k_4[H][CO][O]$$

Considering that $k_4[H][CO][O]$ is practically independent of $T$ and after putting $[O] = [O]_i$ at $t = 0$, we get

$$[H] = \frac{[O]_i}{[O]_i} = \frac{[O]_i}{[O]_i}$$

By substituting this expression in Eq. (1), $T_e - T_1$ is found as a function of $t$, according to

$$\frac{\sum}{[O]_i} = \frac{k_4[H][CO][O]}{[O]_i}$$

The values of $T_e$, $T_1$, i.e. the temperatures corrected for radiation losses may be found from the experimental $T_e - T_1$ curve by extrapolation(9,11). 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 $k_4[H][CO][O]$ is justified. The intercept with the ordinate at $[O] = 0$ of the curve yields the initial O-concentration, $[O]_i$, in absolute measure, according to

$$[O]_i = \frac{\sum}{[O]_i} (T_e - T_1)$$

When chemical equilibrium is fully established in the flame, chemiluminescent reactions do not disturb the thermal population of an excited state (thermochemiluminescence). 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.
relations and the mass balances.

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

FIG. 2b Difference between final equilibrium temperature, $T_{eq}$, and measured local temperature, $T_m$, 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:

$$X + M \rightarrow X + M^*$$  (IX)

and

$$hv + M \rightarrow X + M^*$$  (X)

where $M$ stands for the electronic ground-state particle to be excited and $M^*$ for $K$ in the $3 \Sigma^+$ state or for OH in the excited state $^2 \Sigma^+(v = 0)$ emitting radiation in transitions to the ground state $^3 \Pi(v = 0), ^3 \Sigma^+$, etc.) through process (X), and $X$ is a flame molecule.

If self-absorption is negligible the total emission, $J$, expressed in quanta cm$^{-2}$ sec$^{-1}$ is given by (13,15)

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

Here

$$E = [H] \left\{ k_2 + k_1 k_5 [H_2O] + k_3 \frac{K_a}{K_a + [H_2O]} + k_4 \frac{[\text{OH}]}{[\text{H}_2]} \right\}$$  (7)

and $p$ (the yield factor of resonance fluorescence) = $A, K, E + Z$. Here $A$ is the transition probability and $Z$ is the number of effective quenching collisions per sec, which equals:

$$k_1 [H_2O] + k_2 [H_2] + \ldots + k_5 [X]$$

(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. (6a)). $J_{th}$ follows also from the Boltzmann distribution and the Einstein Transition probability according to

$$J_{th} = \left\{ g[A][M] \exp \left( -\frac{E_{ex}}{K_T} \right) \right\}/Q$$  (8)

where $Q$, $g$ and $E_{ex}$ 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

$$J = J_{th} + p[M] \left\{ [H][OH] - [H][\text{OH}]_{eq} \right\}$$  (9)

The quantities occurring in Eq. (9) can be found from experiments and calculation, except for the factor $p$. The relation between $J$ and $J_{th}$ can be checked experimentally and the absolute value of $p$ can then be found. One plots the experimental value $J$, 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 $J$ curve is thus a curve of shifting along the intensity axis in such a position that the ratio $(J_{th} + J_{exp} - J)/J_{exp}$ 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 $J_{th}$ 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 vs. rise-time for $K_2$- and $C_2H_2$- flames. The data points 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).

*FIG. 4. Suprathermal chemiluminescent emission of OH at 306Å 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 $p$-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 $H_2/O_2/Ar$ and one $H_2/O_2/Ar$ flame.

From this $E$-value Zeegers [15] derived a mean value for $h$ equal to $(7 \pm 1) \times 10^{-3} \text{sec}^{-1}$ at temperatures in the range 1911-2180K. Kaskan has reported a value of $3 \times 10^{-25} \text{cm}^3\text{sec}^{-1}$ at 1900K [20]. This value can be recalculated (by using more recent values for $A$ and $p$) to $(10 \pm 3) \times 10^{-33} \text{cm}^3\text{sec}^{-1}$.

The results in $C,H$-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 $4046/5044$ 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 $K + OH \rightarrow KOH + hv$ [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) experiments 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 $k \cdot X$ equal to $(3.5 \pm 0.3) \times 10^{-25} \text{cm}^3\text{sec}^{-1}$ can be derived [27]. In the $C,H$-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 $C,H$-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 Carabatta and Kaskan [28] 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 $T \approx 1500K$. They found that the reaction $O + O + (M) \rightarrow O_2 + (M) + hv$ is predominant, followed by $H + H + Na (k = 4 \times 10^{-3} \text{cm}^3\text{mol}^{-1}\text{sec}^{-1})$.

C. Distribution of Suprathermal Chemiluminescence 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 [15] which led to the conclusion that continuum emission is completely absent in $H_2$-flames. This is consistent with Dean and Stubbsfield [33], but not with Padley [28]. From these measurements one may conclude that the background emission in $CO$- and $C,H$-flames is only due to the reaction $CO + O + (M) \rightarrow CO_2 + (M) + hv$. (We do not want to go into details with the implication involved in this reaction. It is discussed elsewhere [15], [25].)

The background emission in $CO$- and $C,H$-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 $O$-concentration was found by using a procedure similar to that used in Section IIb.

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/H-flames (Courtesy of Dr. F. Zegers).

The same result has been found at several other wave-lengths in the range from 2300 to 6000 Å. This confirms the reaction mechanism proposed. The radiation originates from excited CO* states that are populated from ground state CO molecules by thermal collisions with flame molecules, as well as by recombinations 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 Eq.(11).

\[ p = \left( \frac{1}{\kappa} + \frac{1}{\kappa} \right) \]

The degree of underpopulation of an excited level can be expressed by introducing the yield-factor \( \kappa \) (Sec IV). \( \kappa \) have \( p = A/h + A \), where \( A \) 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 (\( \kappa_{\text{actual}} \)) and the theoretical (\( \kappa_{\text{thetal}} \)) number of atoms in an excited level as (17)

\[ \kappa_{\text{actual}} = \frac{1}{p} \]

Because of the effect of radiative non-equilibrium on the depopulation of the excited state the line-reversal temperature, \( T_r \), will differ by an amount \( \Delta T \) from the true temperature, \( T_e \). At low metal densities it holds that

\[ \Delta T = \kappa \frac{\kappa}{h} \left( \frac{1}{p} - \frac{1}{p} \right) \]

\[ \kappa_{\text{actual}} = \kappa_{\text{thermal}} + \kappa_{\text{radiative}} \]

for all relevant p-values in our flames.

\[ \frac{\kappa_{\text{actual}}}{\kappa_{\text{thermal}}} = 1 + \frac{\kappa_{\text{radiative}}}{\kappa_{\text{thermal}}} \approx 1 \]

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

The value of \( p \) can be measured in actual flames by 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 in (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 305 Å) for the different flame gas components (10,19).

From our results it appeared that atoms are not effective in quenching (\( p \approx 1 \)). The most effective quenchers are the diatomic and triatomic molecules. Some specific \( \kappa_{\text{qu}} \) values for the Na D-doublet at T = 5000 K are

\[ \kappa_{\text{qu}} (Na - Ar) = \kappa_{\text{qu}} (Na - CO) \approx 0 \]

For 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 in (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 305 Å) for the different flame gas components (10,19).

From our results it appeared that atoms are not effective in quenching (\( p \approx 1 \)). The most effective quenchers are the diatomic and triatomic molecules. Some specific \( \kappa_{\text{qu}} \) values for the Na D-doublet at T = 5000 K are

\[ \kappa_{\text{qu}} (Na - Ar) = \kappa_{\text{qu}} (Na - CO) \approx 0 \]

For 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 in (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 305 Å) for the different flame gas components (10,19).

From our results it appeared that atoms are not effective in quenching (\( p \approx 1 \)). The most effective quenchers are the diatomic and triatomic molecules. Some specific \( \kappa_{\text{qu}} \) values for the Na D-doublet at T = 5000 K are

\[ \kappa_{\text{qu}} (Na - Ar) = \kappa_{\text{qu}} (Na - CO) \approx 0 \]

For 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 in (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 305 Å) for the different flame gas components (10,19).

From our results it appeared that atoms are not effective in quenching (\( p \approx 1 \)). The most effective quenchers are the diatomic and triatomic molecules. Some specific \( \kappa_{\text{qu}} \) values for the Na D-doublet at T = 5000 K are

\[ \kappa_{\text{qu}} (Na - Ar) = \kappa_{\text{qu}} (Na - CO) \approx 0 \]

For 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).
e\text{lectronic 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 its composition of burnt gases are determined. Therefore one may readily derive the value of \( \Delta T \). Conversely from the measured value of \( \Delta T \), 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.

\[ T_e = (13) \]

From Fig. 7 we find \( \Delta T = 8 K \pm 3 K \). The p-value of this flame is known: \( p = 0.32 \). From this value we may calculate (cf. Eq. 10): \( \Delta T = 80 \pm 3 K \), 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, provided that p is not too small.[17]

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

From the figure we conclude that with high solution concentration \( \Delta T \) varies as \((M)^2\) as predicted by theory for a Lorentzian line shape.

\( \Delta T = M^2 \) (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 processes, are equilibrated at the local temperature \( T \), then \( m \) and \( s \) are related by:

\[ m = \frac{2}{3} M^2 + e \] (11)

Here \( m \) and \( s \) represent the rate constants of the ionization and recombination reactions, respectively.

\[ q = s(M)^2 + \frac{dm}{dt} \] (14)

where \( q \) = recombination 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 \( x = vt \) and by substituting \( \tilde{M} = M + M^2 \), where \( \tilde{M} \) = \( M + M^2 \) and \( q = 2M \)

\[ \frac{dM}{dt} = s(M) - s(M + M)^2 \] (15)
\[ m_{th}(T) = \frac{m}{I(T)} \tag{16} \]

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

If these equilibration conditions were locally fulfilled throughout the flame and if \( m \) and \( m_{th} \) were infinitely large, then the fraction of ionized metal would correspond to Saha-equilibrium at any position of the flame at the prevailing temperature.

From Eqs. (15) and (16) we find
\[ \frac{\text{d}M}{\text{d}t} = m_{th} \left( 1 - \frac{(H - M)}{I(T)} \right) \tag{17} \]

When determining photometrically the variation in atomic metal content with height (or rise-time) for a certain total metal content \( M \) 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: Measured atomic metal content as a function of height above the blue cones in a CO-flame (\( T = 2500 \text{ K} \)). The dotted curves represent the corresponding Saha curves.](image)

In the construction of these "theoretical Saha-curves" we used the fact that they should virtually intersect the corresponding experimental curves at the point where the latter attain their minimum values, i.e., where \( \text{d}M = 0 \) (and thus \( \text{d}M = 0 \)). 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 \( M \) or the ratio \( M/N \) (in any point of the experimental curve) for the metal solution sprayed. The absolute values of \( M \) is found from self-absorption measurements (5-6), that of \( M/N \) is based on ionization suppression measurements in the minimum point of the experimental \( \text{d}M/\text{d}t \) curve.

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 usec. 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:
\[ \frac{\text{d}M}{\text{d}t} = m_{th} \left( 1 - \frac{(H - M)}{I(T)} \right) \tag{16} \]

From the experimental \( M \)-curve, \( m_{th} \) the known absolute value of \( M \) and the measured temperature profile one calculates \( m_{th} \) from this equation. The results obtained downstream the temperature maximum for several CO/O,N 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 residual temperature at the point where \( m_{th} \) was determined.

![Fig. 10: Values of \( m_{th} \) as a function of \( T^{-1} \).](image)

The \( m_{th} \) values plotted are not corrected for the contribution of thermal chem-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
\[ m_{th} \propto \sqrt{\frac{u}{N \cdot Q_{ion}}} \exp \left( -\frac{E_i}{K} \right) \tag{19} \]

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

Since a flame contains molecules of various kinds \( u \) and \( Q_{ion} \) refer to some sort of average value. In
our flames $N$, CO, and CO are the most important constituents. Assuming in first approximation that the $\tilde{Q}$ values vary with the quasicontinuous diameters of the molecules and knowing the quantitative composition of the burnt gases, we may calculate the variation of the average value $\tilde{Q}/\tilde{u}$ in the different flames. The distribution of the relevant molecules is in thermal equilibrium and thus 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 $H$, $O_2$, $N_2$ flames support very nicely the behavior of $\tilde{Q}$ as a function of $T^*$ 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 0.26$eV$, is most important. This variation appeared to be at most $\pm$ 4% for Na, K and Cs, respectively, so we may neglect this variation in the flames considered.

For simplification we assume the flame consists of $N$, $O_2$, $H_2$, $N_2$ molecules at constant temperature, $T$, throughout the subvolume considered. The vibrational energies available (vibrational, rotational, translational and excitation energies) are supposed to be distributed according to the Boltzmann formula. The discrete vibrational energy levels of the molecules are approximately equidistant ($h_0 = kT$). 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 and ion possesses a virtually infinite number of vibrational energy levels with energy $E_v$. In principle the occupation of these levels obeys the Maxwell Boltzmann Law. For simplification we suppose that $Q_{\text{ion}}$ is constant for any value of $J$ and is independent of the environment of the molecule and of the kind of energy transferred. This $Q_{\text{ion}}$ refers to some sort of average value. Under the assumption that the ionization of the atom occurs at $E_j + E_v \geq E_1$ where $E_1$ is the first excited energy level of the atom.

In this equation the infinite summation $\sum_{J=0}^{\infty} \frac{Z_{\text{ion}}}{\text{v}^n}$ occurs. In order to circumvent this difficulty we split this summation in two parts: one summation over the excitation levels with $E_v + E_1 > kT$ (0 $\leq J < n$) 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 the $Q_{\text{ion}}$ values from the $Q_{\text{vib}}$ values experimentally found according to Eq. (20). It should be noted that if we had chosen $E_v$ smaller or larger by $kT$, the $Q_{\text{ion}}$ 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 $E_1$, 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. 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 equilibration with respect to the ion 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 \( s \)-values at \( T = 2500 \, \text{K} \) we calculate now the following (under-limiting) values of \( Q_{\text{ion}} \):

\[
Q_{\text{ion}}(\text{Na}) = 9.69 \times 10^{-12} \text{ cm}^2, \quad Q_{\text{ion}}(\text{K}) = 9.29 \times 10^{-12} \text{ cm}^2, \quad \text{and} \quad Q_{\text{ion}}(\text{Cs}) = 9.9 \times 10^{-12} \text{ cm}^2.
\]

The order of magnitude of these values compare fairly well to that of gas-kinetic cross-sections being in the order of \((30-80) \times 10^{-12} \text{ cm}^2\). While comparing \( Q \)-values with gas-kinetic cross-sections the quenching cross-sections (cf. Sec. IV) amounting to \((9-100) \times 10^{-12} \text{ cm}^2\).

It should be noted that the \( Q \)-values increase in the sequence \( \text{K} < \text{Na} < \text{Cs} \), 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 \( Q \)-values with gas-kinetic cross-sections. We have only considered \( n \)-molecules. The \( Q_{\text{ion}} \)-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 \( m \)-values for \( \text{Na} \), \( \text{K} \) and \( \text{Cs} \) at \( 2500 \, \text{K} \) amounting to \((9.0, 190, 400) \times 10^{-16} \text{ sec}^{-1} \), respectively, may be compared with those obtained by Jensen and Padley(39). They found the following values: \((7.2, 280, 4000) \times 10^{-16} \text{ sec}^{-1} \), respectively, for \( \text{Na} \), \( \text{K} \) and \( \text{Cs} \). We have no explanation for the discrepancy in the case of \( \text{Cs} \).

For comparison we give the results for \( m(\text{Sr}) \) in the CO-, O-, N-flames(43), for temperatures ranging from \( 2400 \) to \( 2600 \, \text{K} \) the \( m \) (Sr) varied from \((1.9 \, \text{to} \, 11.8) \times 10^{-13} \text{ sec}^{-1} \). Herefrom we derive the following \( m \) (Sr) value of about \( (3.1 \times 10^{-12}) \text{ sec}^{-1} \) (at \( T = 2500 \, \text{K} \)), comparable to the values found for \( \text{Na} \), \( \text{K} \) and \( \text{Cs} \).

From the \( m \)-values we may derive the corresponding gas-kinetic cross-sections decrease in the sequence \( \text{Na} - \text{K} - \text{Cs} \), i.e. with decreasing ionization potential. This holds also when the ionization proceeds as suggested in our work.

The probability of this reaction may be enhanced by considering this reaction to be composed of two successive steps \( \text{CO} + 0 + \text{X} \rightarrow \text{CO}_2 + \text{X} \) (where \( \text{X} \) is a flame molecule) followed by: \( \text{X} + \text{Na} \rightarrow \text{Na} + \text{e} \). Similar two-step processes have been discussed elsewhere(12,15,17) in connection with the suprathermal excitation of alkali atoms. It should further be noted that Wigner's Rule is obeyed in reaction (XVI) when \( \text{M} \) is an alkali metal.

The actual \( T \)-content in the flame can now be derived from the temperature profile in the flame and \([\text{CO}] \approx [\text{CO}], [\text{CO}]_\text{eq} \) (cf. Sec. IIIa). We may neglect \( [\text{CO}]_\text{eq} \) (cf. Sec. IIIa). We may formally write for the \( m \)- and \( s \)-values actually found: \( m = m_\text{th} + m_\text{exc} \) and \( s = s_\text{th} + s_\text{exc} \). It is now assumed that:

\[
m_\text{exc} = \left[ [\text{CO}]_\text{eq} - [\text{CO}]_\text{eq} \right] \cdot m_\text{th}
\]

and likewise:

\[
s_\text{exc} = \left[ [\text{CO}]_\text{eq} - [\text{CO}]_\text{eq} \right] \cdot s_\text{th}
\]

Since \([\text{CO}]_\text{eq} \approx [\text{CO}]_\text{eq} \) (cf. Sec. IIIa), we may neglect \( [\text{CO}]_\text{eq} \) (cf. Sec. IIIa). We may now derive:

\[
m_\text{th} (\text{K}) = \left( [\text{CO}]_\text{eq} - [\text{CO}]_\text{eq} \right) \cdot m_\text{th}
\]

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

The actual \( T \)-content in the flame can now be derived from the temperature profile in the flame and the \( [\text{CO}] \approx [\text{CO}], [\text{CO}]_\text{eq} \) (cf. Sec. IIIa). \([\text{CO}]_\text{eq} \) 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 \( m \)-values experimentally found for \( \text{K} \) and \( \text{Cs} \) as \( f \text{unction of} \, [\text{CO}]_\text{eq} \), we find in good approximation a straight line through the origin(6). This is a nice experimental confirmation for the chemi-ionization

\[\text{TABLE 2. COMPARISON OF EXPERIMENTAL} \, s_\text{th} \text{-VALUES (1} \times \text{SEC}^{-1}) \text{ WITH LITERATURE DATA}^\dagger\]

<table>
<thead>
<tr>
<th>Salts</th>
<th>( \text{Air-C}_2\text{H}_2 , \text{Flame}^* )</th>
<th>( \text{H}_2\text{O}_2 , \text{Flame} )</th>
<th>( \text{Air-C}_2\text{H}_2 , \text{Flame} )</th>
<th>( \text{H}_2\text{O}_2 , \text{Flame} )</th>
<th>( \text{CO}_2/\text{H}_2 , \text{Flame} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIO</td>
<td>( (6.5 - 9.0) \times 10^{-9} )</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>LIO</td>
<td>( (7.8 - 9.2) \times 10^{-9} )</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>LIO</td>
<td>( (1.9 - 2.8) \times 10^{-9} )</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>LIO</td>
<td>( (3.1 - 4.0) \times 10^{-9} )</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>LIO</td>
<td>( (0.18 - 0.25) \times 10^{-9} )</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>LIO</td>
<td>( (0.17 - 0.25) \times 10^{-9} )</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

* for metal concentrations in the range \( 0.01 - 0.1 \, \text{N} \)}
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

\[ M + H_2 \rightarrow MO + H \] (XVII)

and/or

\[ M + OH \rightarrow MO + H \] (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 concentrations 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, 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 \[ H + H_2O \rightarrow OH + H_2 \] (sec. Sec. (III)).

Since the greater part of the alkaline-earth metal is present in the flame as oxide (6/7) 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 2000 to 5500K) 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 varied from 0.8 to 4.5 cm
(ii) the flame temperature (and flame gas composition) was varied

by supplying additional water vapor.

The results compare satisfactorily with other recent data from flame photometric work in the literature (7/8/9). 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 equilibrium of the dissociation reaction (6/7). We want to discuss the reactions that may explain this outcome:

The direct dissociation and recombination reaction

\[ MO + X \rightarrow M + O + X \] (XIX)

would require a third body X. It seems unlikely, 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 process involving intermediate (vibrationally excited) states of the oxide molecule, might enhance considerably the over-all probability of a dissociation 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

\[ CO + CO \rightarrow M + CO_2 \] (XX)

CO- and CO_2 contents virtually equal their equilibrium values, regardless of the deviation in atomic O-content (6/7) (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

\[ H_2 + CO \rightarrow H_2O + CO \] (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

\[ CO + O \rightarrow CO_2 \] (Sec. Sec III), which is still believed to be possible, however. Possibly the formation of alkaline-earth atoms in an excited triplet state through reaction (XII) should be considered. In this case the change in enthalpy amounts to +20, +26 and +29 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 3n 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 $^3\Sigma$ state of the lower level (55-58). This singlet state possibly correlates upon dissociation with ground state atoms $^2\Sigma$ or $^2\Pi$ 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, H$_2$O, and H$_2$(OH), might be present in the flame. It's 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-containing flames has been obtained from photographic measurements (68-71). A recent publication of Sugden and Schofield (72) suggested that (MOH) might be much more important than (MOH) in H$_2$/O$_2$ flames.

Our spectrographic observations of the alkaline-earth spectra in dry and moist CO/O$_2$/N$_2$-flames, C$_2$H$_2$/O$_2$/N$_2$, and C$_2$H$_2$/H$_2$O$_2$/N$_2$-flames 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$_2$-, H$_2$-, and C$_2$H$_2$-flames.

The absolute value of the excitation energy of a molecular band, $E_{21}$, can be determined as follows: The difference of the $E_{21}$ values of two bands (measured at the band heads) of the same alkaline-earth can be found from the equation. (This difference is independent of content and dissociation energy).

$$E_{21}^{(2)} - E_{21}^{(1)} = k \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \ln \left( \frac{\left[ MO \right]^{(1)}}{\left[ MO \right]^{(2)}} \right) \left( \frac{\left[ M \right]^{(2)}}{\left[ M \right]^{(1)}} \right) \left( \frac{T_2}{T_1} \right)$$

where $T_1$ and $T_2$ are two (different) flame temperatures and $\left[ MO \right]$ and $\left[ M \right]$ 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 $E_{21}$ can be determined following the method applied by Huldt and Lagerqvist (60,62). The band emission (corrected for limitation) is measured as a function of flame temperature, with a given metal solution sprayed. The corresponding meter deflection, $u_{21}$, satisfies the following relation

$$u_{21} \propto \left[ MO \right]^{(1)} \exp \left(-E_{21}/kT \right)$$

where $l$ is the thickness of the colored flame part, $\left[ MO \right]$ the concentration of molecules MO, and $E_{21}$ the excitation energy. By plotting $\ln u_{21}$ versus $(kT)^{-1}$ (after correcting for the possible change in $l$ and $\left[ MO \right]$ with varying temperature) we find $E_{21}$ for the band considered from the slope of the curve. In order to correct for the variations in $l$ and $\left[ MO \right]$ upon variations in temperature, we measured the corresponding variations in the $\Delta$-bands doublet emission. Herefrom we derive after correcting for the varying temperature, the relative change in the product $\left[ MO \right]/\left[ M \right]$ refer to the total element concentration in cm$^{-2}$ present in the flame part investigated. It should be remarked that not only $\left[ MO \right]/\left[ M \right]$ may vary, but also the ratio $\left[ MO \right]/\left[ M \right]$. The variations in $\left[ MO \right]$ 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.

1. 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).

2. The actual oxygen concentration is supposed to be equal to the equilibrium concentration.

3. 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 to 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 (1) 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.

From the straight lines in Fig. 11 we conclude that the population of the excited states...
involved is thermal indeed. The \(E_{\mathrm{MO}}\)-values derived from this graph are given below (See Table 3). It should be noted that the \(E_{\mathrm{MO}}\)-values found were used for the derivation of dissociation energies, \(D^0\), of the alkaline-earth oxides from line/band ratios. Since these \(E_{\mathrm{MO}}\)-values appeared to agree very well with the \(D^0\)-values derived in an independent method (6,7), the \(E_{\mathrm{MO}}\)-values are reliable ones. Furthermore their differences are in good agreement with the energy differences found independently according to Eq. (26) (See Table 4). Since in our CO-flames only MO-molecules are present, we may be certain that our \(E_{\mathrm{MO}}\)-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 (1) and (4) we may conclude:

1. The same emitters, i.e. oxide molecules are most likely responsible for the visible alkaline-earth oxides from line/band ratio indication 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.

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

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

<table>
<thead>
<tr>
<th>Metal</th>
<th>Band Head in (\AA)</th>
<th>(E_{\mathrm{MO}}) in (C_2H_2)-Flame*</th>
<th>(E_{\mathrm{MO}}) in (H_2)-Flame**</th>
<th>(E_{\mathrm{NO}}) in CO-Flame*</th>
<th>(E_{\mathrm{NO}}) in (C_2H_2)-Flame**</th>
<th>(E_{\mathrm{NO}}) in (H_2)-Flame**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>5475</td>
<td>4.47 ± 0.28</td>
<td>4.96 ± 0.30</td>
<td>3.14 ± 0.04</td>
<td>3.21 ± 0.10</td>
<td>3.14 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>6020</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>6060</td>
<td>3.97 ± 0.24</td>
<td>4.72 ± 0.28</td>
<td>2.99 ± 0.03</td>
<td>3.02 ± 0.10</td>
<td>2.98 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>6540</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>4873</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5087</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5230</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5350</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
* cf. lit. (62)  
** cf. lit. (60)  
++ cf. lit. (6,7)

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

<table>
<thead>
<tr>
<th>Metal</th>
<th>Band Heads in (\AA)</th>
<th>CO-Flame</th>
<th>(C_2H_2)-Flame</th>
<th>(H_2)-Flame</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>(E_{5475} - E_{6020})</td>
<td>-0.12 ± 0.05</td>
<td>-0.14 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(E_{5475} - E_{6220})</td>
<td>0.22 ± 0.03</td>
<td>0.14 ± 0.07</td>
<td>0.13 ± 0.05</td>
</tr>
<tr>
<td>Sr</td>
<td>(E_{6060} - E_{6450})</td>
<td>-0.15 ± 0.05</td>
<td>0.02 ± 0.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(E_{6060} - E_{6660})</td>
<td>0.13 ± 0.03</td>
<td>0.12 ± 0.01</td>
<td>0.13 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>(E_{6060} - E_{6820})</td>
<td>-0.07 ± 0.05</td>
<td>0.18 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>(E_{5350} - E_{4873})</td>
<td>-0.49 ± 0.10</td>
<td>-0.35 ± 0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(E_{5350} - E_{5087})</td>
<td>0.47 ± 0.04</td>
<td>0.52 ± 0.05</td>
<td>0.46 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>(E_{5350} - E_{5230})</td>
<td>-0.06 ± 0.01</td>
<td>-0.10 ± 0.03</td>
<td></td>
</tr>
</tbody>
</table>