Photometric Investigations of Alkali Metals in Hydrogen Flame Gases. IV. Thermal and Chemiluminescent Effects Produced by Free Radicals

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Photometric investigations of alkali metals in hydrogen flame gases

IV. Thermal and chemiluminescent effects produced by free radicals

BY P. J. PADLEY AND T. M. SUGDEN

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The intensity of emission of the sodium D-lines has been observed as a function of height above the burner for traces of sodium salts added to premixed hydrogen + oxygen + nitrogen flames burning at atmospheric pressure. A specially constructed Mèker burner was used, giving an almost flat reaction zone. Flames in which the final temperatures of the burnt gas ranged from 1400 to 2500 °K were used.

At the higher final temperatures, the intensity showed a rapid rise at the reaction zone, followed by a more steady rise to a constant value. This has been interpreted as a thermal effect, the bulk temperature of the flame gases increasing by significant amounts as a result of heat released by the recombination reactions

$$H + H + X \rightarrow H_2 + X,$$

$$H + OH + X \rightarrow H_2O + X.$$
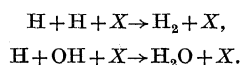
Values of the mean velocity constants of these ternary reactions have been deduced, and are in agreement with independent estimates.

At the lower final temperatures, there is a sharp peak of intensity at the reaction zone, followed by a decrease towards a steady value. This has been interpreted as a chemiluminescent effect, the sodium being excited by ternary reaction with two free radicals:

$$H + H + Na \rightarrow H_2 + Na^*,$$

$$H + OH + Na \rightarrow H_2O + Na^*.$$
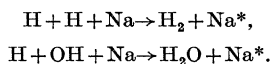
The decay of chemiluminescence with height in the flame gases accords with the known decreases of the concentrations of atomic hydrogen and hydroxyl. Relative and absolute velocity constants for these processes are derived and discussed.

1. INTRODUCTION

Although the kinetics of many of the reactions involving free radicals in the reaction between hydrogen and oxygen have been satisfactorily resolved by studies in static systems at low temperatures (see, for example, Lewis & von Elbe 1951; Nalbandyan & Voyevodsky 1949), there is as yet relatively little in the way of a complete quantitative link between the results of work in these systems and the results of work on burner flames of hydrogen and oxygen. One advantage of the study of the latter kind of system is that it is relatively easier to measure the concentrations of free radicals (atomic hydrogen and oxygen, and hydroxyl) than in the lower temperature work, since in general they are higher in flames, and since burner flames are steady-state systems in which the time scale for reactions may be converted into a distance scale in the direction of flow of the gases. The value of a knowledge of the concentrations of free radicals in the development of the theory of flame reactions is obviously of the greatest importance.

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Various methods have been developed for the detection and estimation of atomic hydrogen and hydroxyl in flame gases, these radicals being in general the most abundant. They may be summarized briefly.

(i) Atomic hydrogen (and probably simultaneously hydroxyl) may be detected by the luminescence produced on surfaces introduced into the flame gases (Arthur & Townend 1954). This occurs because of recombination of radicals at the surface, with evolution of heat. Colour changes of certain solid oxides have also been used in this connexion (Arthur 1949), as well as the anomalous temperatures obtained with bare thermocouples inserted into flames (David & Mann 1947). These methods do not readily lend themselves to quantitative measurements.

(ii) Hydroxyl radicals may be studied by observations on their characteristic spectrum, either in absorption or in emission, in the region of 3000Å. This method has been used to obtain concentrations of hydroxyl in hydrogen flames (Kondratieva & Kondratiev 1946), and also to investigate anomalous excitation of hydroxyl (emission) in reaction zones (Gaydon 1957).

(iii) Flame photometric measurements of various trace substances, dispersed molecularly in the flame gases, may be used. These substances, usually metallic elements or their compounds, interact with the free radicals of the flame gases to extents which may be deduced from the measurements, and from which the concentrations of the free radicals may be inferred. Parts II and III in this series (Bulewicz, James & Sugden 1956; James & Sugden 1958) deal with such measurements for atomic hydrogen and for hydroxyl, and similar work has been described in other publications (Sugden 1956; Bulewicz & Sugden 1956a,b).

One of the principal results of this last group of studies has been to demonstrate that in the burnt gas of hydrogen + oxygen + nitrogen mixtures, from a Mèker burner, there is strong general evidence for radical concentrations in considerable excess of the equilibrium values, as calculated on the basis of fuel-oxidant composition and the measured temperature of the burnt gas. The burnt gas, however, has certain steady-state properties, determined by rapid balanced reactions such as

$$H_2O + H \rightleftharpoons H_2 + OH,$$
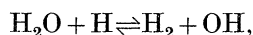
which are able to maintain certain ratios of radical concentrations, in this case [H]/[OH], at their equilibrium values. The approach towards equilibrium is determined by much slower ternary processes such as

$$H + H + X \rightarrow H_2 + X,$$
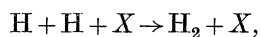
where X is a third body. The degree of advancement of this latter type of reaction varies significantly with the vertical distance from the primary reaction zone, and it has been possible to use the flame photometric methods to obtain some information about the velocity constants of such reactions as a result of this.

The present work began as an attempt to apply the methods of flame photometry nearer to the reaction zone of the flame than had previously been possible. The relatively large height (2 to 3 mm) of the cones at the Mèker burner used in the earlier work made measurements valueless at points nearer than 1 cm to the burner, on account of lack of uniformity of the cross-section of the column of burnt gas.

A new burner has been designed giving a flame with cones only about $\frac{1}{2}$ mm in height, which approaches, but does not reach, the degree of flatness which has been reached with flames on sintered metal burners (Botha & Spalding 1954). These latter were not used because of the difficulties of adding sprays of salt solutions to the unburnt gas.

Two new effects, both of considerable interest, have been detected by studying, with this burner, the luminescence from traces of sodium added to hydrogen + oxygen + nitrogen mixtures. They are:

(i) A notable decrease in the flame temperature (which can be as great as 300 °C) on approaching the reaction zone from above. This effect arises from, and can be correlated with, the marked increase in concentration of free radicals towards the reaction zone. The release of heat accompanying the recombination of the radicals can be used to estimate their concentration.

(ii) Marked chemiluminescence of sodium in the reaction zone and immediately above it, in the case of gases whose final temperatures were below about 1800 °K (the total range of temperatures used was about 1500 to 2500 °K). This effect proves to be consistent with excitation of sodium by reactions such as

$$Na + H + H \rightarrow Na^* + H_2,$$
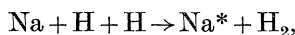
followed by emission from the sodium atoms. It is obscured at higher temperatures by the high level of thermal emission, which is used to study the phenomenon (i) above.

2. EXPERIMENTAL

The burner used for producing flames of premixed hydrogen, oxygen and nitrogen is shown in figure 1. The central 'experimental' flame, of diameter 1 cm, is burnt above a core of 100 stainless-steel hypodermic tubes (Accles and Pollock gauge 20), tightly soldered together. The internal diameter of the tubes is 0·055 cm. This gives primary cones not more than $\frac{1}{2}$ mm in height, and an excellent laminar flame. It is surrounded by a shielding flame fed from B (figure 1) with a mixture of the same composition. This flame is also laminar, and serves to protect the inner flame from the effects of indrawn air, and to eliminate discontinuities at the boundary of the inner flame. Additional shielding is provided by an outer flame supplied from C with the same mixture. This part of the burner is slightly recessed below the level of the inner portion. Provision was also made for a protective shield of nitrogen outside this, but was found in general not to be necessary. Excellent shielding of the 'experimental' flame up to a height of 10 cm from the burner was obtained in most cases.

The flames were classed into 'families', as in the previous work, based on the composition of the unburnt gas. Each family was characterized by a subscript numeral giving the unburnt N_2/O_2 ratio by volume; this varied from 3 to 9. A family contained 5 flames, characterized by H_2/O_2 ratios (unburnt, by volume) of 2·5, 3·0, 3·5, 4·0, 4·5, denoted by F, K, P, U, Z, respectively. This gave a range of final flame temperatures ranging approximately from 1500 to 2500 °K, as measured by the sodium D-line reversal method (Gaydon & Wolfhard 1953). The rate of supply of

the gases to the burner was changed progressively through the range of flames so as to compensate for a sixfold change in burning velocity. Maximum flow through the central flame was 0·5 cu.ft./min (unburnt at room temperature), and the shield flames consumed about four times as much gas mixture as the central flame.

The flame photometric system for measurement of the light emitted from selected spectral regions was very similar to that described in part I (James & Sugden 1955). An image of the inner flame was focused on to a sector disk rotating at 600 c/s. Two front-surfaced plane mirrors were arranged in conjunction with a second lens so as to form a further image rotated through 90°. This image was focused on the vertical entrance slit of either a Hilger E. 3 medium quartz spectrometer or a Rutherford prism monochromator constructed in the laboratory. By control of the entrance slits of the monochromator or by alteration of the conjugate points of the optical system the light from a narrow horizontal strip of the flame gases, variable in height
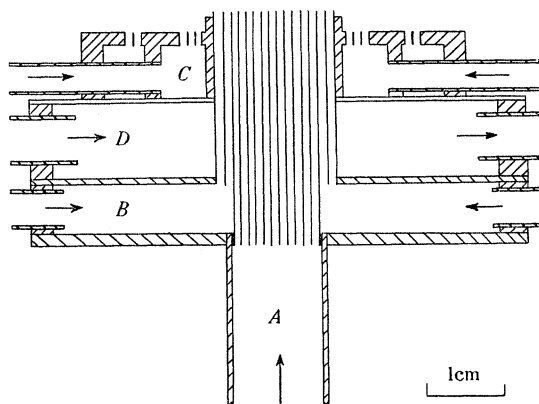

FIGURE 1. Diagrammatic vertical cross-section of burner. *A*, flame to be studied, containing additives; *B*, laminar flow shield; *C*, outer shield; *D*, water cooling.

from 1 cm to 0·1 mm, could be examined. Detection in both cases was with an IP 28 photomultiplier tube, the signal being converted into a d.c. micro-ammeter reading by means of a low-noise homodyne amplifier synchronized by the chopping disk. Spectral resolution was of the order of 1 Å in the vicinity of the sodium *D*-lines, on which most of the measurements were made, but the slits in front of the photo-multiplier were widened sufficiently to cover both lines of the sodium doublet. The overall spatial resolution was restricted by the finite thickness of the inner column of flame gases to about $\frac{1}{2}$ mm of height.

The additives (usually sodium salts) were supplied to the innermost flame as fine sprays of dilute aqueous solutions from an atomizer operated by the nitrogen supply. Such sprays pass successfully through the fine tubes of the burner without causing clogging. Experiments with burners with sintered disks proved to be unsatis-factory on this account, so that the degree of flatness in the flame which might have been obtained by using them had to be sacrificed. All solutions used in the atomizer were sufficiently dilute not to give appreciable self-reversal of the light examined.

3. Results

Using a constant spray of $0 \cdot 001$ M sodium chloride in the supply to the central flame, the D-line emission from a section of the burnt gas $0 \cdot 5$ mm in height was examined as a function of height (and hence of time from leaving the reaction zone) for all the flames. A selection of the results, showing the emitted intensity as a function of time from leaving the reaction zone, is shown in figure 2. The vertical velocity of the burnt gas fell into the range of 5 to 20 m/s, the higher velocities being used for hotter flames. The limiting resolution in time obtained ranged from about $100 \, \mu s$ for the lower velocities to $25 \, \mu s$ for the higher ones. Intensities are directly
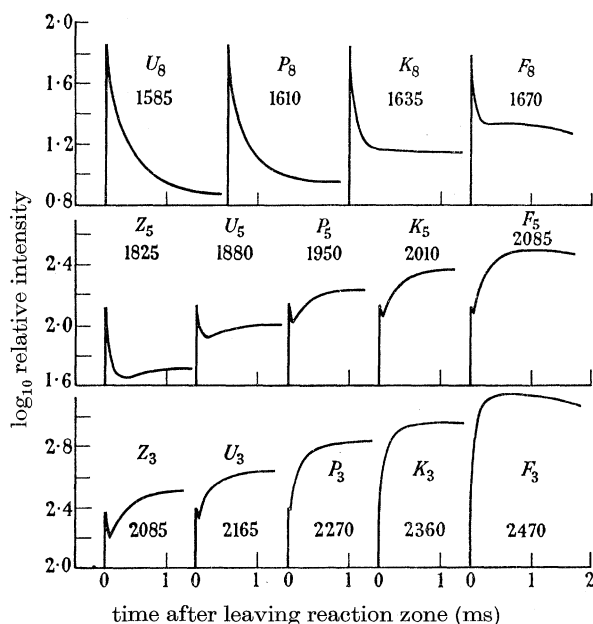

FIGURE 2. Variation of sodium D-line intensity with time from primary reaction zone. F, K, P, U, Z denote flames with unburnt H_2/O_2 volume ratios of $2 \cdot 5$, $3 \cdot 0$, $3 \cdot 5$, $4 \cdot 0$, $4 \cdot 5$, respectively. The subscript numeral denotes the unburnt N_2/O_2 volume ratio. The temperatures quoted are T_f, the line-reversal temperature reached where the curves become nearly horizontal.

proportional to the concentration of excited sodium, which is always a small proportion of that of the total free atomic sodium present. In all cases, after about 1 ms from leaving the reaction zone, a nearly steady intensity is reached. This region of constant intensity is that examined in part I; the emission here is considered to be thermal in nature, and in this region reactions in the flame gases are so near to equilibrium that further possible changes in composition are too small to have a measurable effect on the temperature. The sodium D-line temperatures for this constant region are indicated in figure 2. Such temperatures will be referred to as T_f. There is a marked trend in the shape of the curves as T_f moves from high to low values. At the highest values of T_f, a very rapid rise in intensity at the reaction zone is followed by a further more gradual increase over a period of about 1 ms. On the other hand, at low T_f, the almost instantaneous rise at the reaction zone is

followed by a near discontinuity, with subsequent decrease towards a steady intensity. At intermediate temperature an obvious compound of these two effects occurs.

Although the observation of the sharp peak may be limited by the spatial resolution of the measuring instrument, the peak appears to have a nearly constant intensity for given N_2/O_2 in the gas supply. Further, its height varies by less than a factor of four over the whole range of flames, while the final intensity, which corresponds with T_f, varies by a factor of about 400. Evidence will be given in §4 below for the following general interpretation of the results. Both the high-temperature effect (i) and the low-temperature effect (ii) are considered to arise from the presence of excess free radicals H and OH, operating in different ways under the two sets of conditions.

(i) At high temperatures the overwhelming bulk of the emission at all points is thermal in origin, the rise in temperature with increasing height (or time from the reaction zone) occurring because of heat released by the recombination of the excess radicals.

(ii) At low temperatures, the thermal emission (now very much smaller) is swamped by chemiluminescence, produced by excitation of sodium atoms at ternary collisions with two free radicals. This chemiluminescence decays as the concentration of radicals falls off with increasing height as a result of recombination.

A few further experiments with some bearing on the general validity of this interpretation will be reported before a detailed discussion is presented. It is only legitimate to use the intensity of the D-lines, in the absence of self-reversal, as a comparative measure of the excitation temperature at various points in the flame gases if the concentration of sodium in the ground state is independent of height. This will not be true if significant amounts of any compound of sodium are present to an extent dependent on height. Partial, rather than complete dissociation of the added salt might cause this; sodium hydroxide, the only new compound likely to be formed in the flame gases, is known (part I) not to be significant. This criticism does not apply to line-reversal measurements of temperature, which depend only on the ratio of excited to unexcited sodium. Figure 3 shows plots of the excitation temperature of sodium in a number of flames; the open circles represent results obtained by D-line reversal, the full circles represent results based on the intensity of emission only, using dilute solutions of sodium chloride. The two kinds of observation are scaled together at the highest temperature obtained by the line-reversal method in each case. The correlation over the rest of the range of height is very good. Since there is strong evidence that at the limiting temperature T_f the decomposition of the added salt is complete, it is justifiable to assume that it is also complete down to less than 1 mm above the reaction zone, i.e. that dissociation is complete within $100 \mu s$ from entering that zone. Figure 4 shows an intensity plot for four different salts of sodium, and only in the case of the very stable sulphate is there any serious evidence of incomplete dissociation at measurable times. It is therefore legitimate to use the intensities for any one flame, suitably scaled by one line-reversal measurement, as an exponential measure of the excitation temperature of sodium. This greatly facilitates the work, since much more time would be necessary for line-reversal readings at all points.

Observations have also been made on the intensity of the CuH $(0,0)$ band in emission at $4288\,\text{Å}$, produced from traces of added copper salts, and on the intensity of the sodium continuum in the region of $4500\,\text{Å}$. The former of these has been shown to correlate fairly directly with the concentration of atomic hydrogen in flame gases (Bulewicz & Sugden 1956 a), and the latter with the concentration of hydroxyl
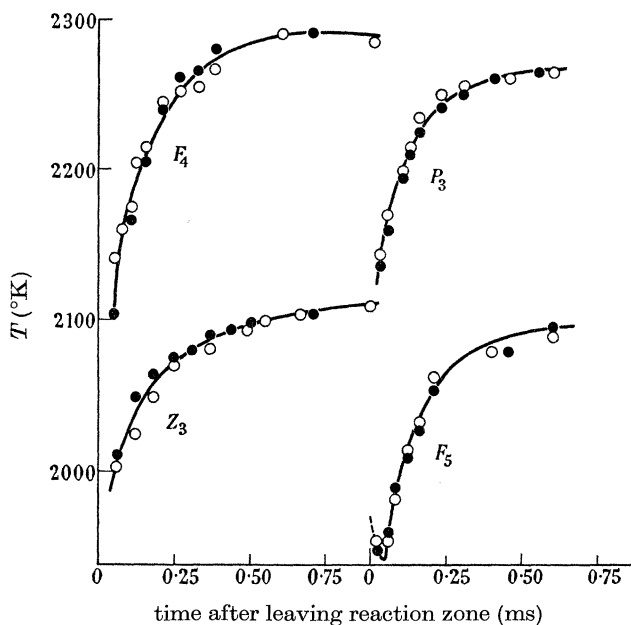

FIGURE 3. Temperature of flame gases based on sodium D-line reversal ($\bigcirc$), and on intensities of emission of sodium D-lines ($\bullet$) as functions of time from leaving the reaction zone. Results for the two methods are scaled together at the highest reversal temperature observed in each case.
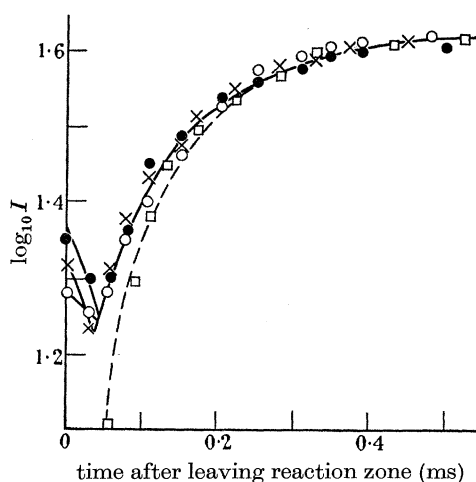

FIGURE 4. Comparison of the intensities of the sodium D-lines for various sodium salts added, as functions of time from the reaction zone. $\times$, NaCl; $\bullet$, NaOH; $\bigcirc$, $Na_2S_2O_3$; $\square$, Na_2SO_4. Flame U_3.

(James & Sugden 1958). Examples of the results are shown in figures 5 and 6, respectively, plotted as reciprocal of intensity against time, and are seen to be good straight lines almost to the reaction zone.
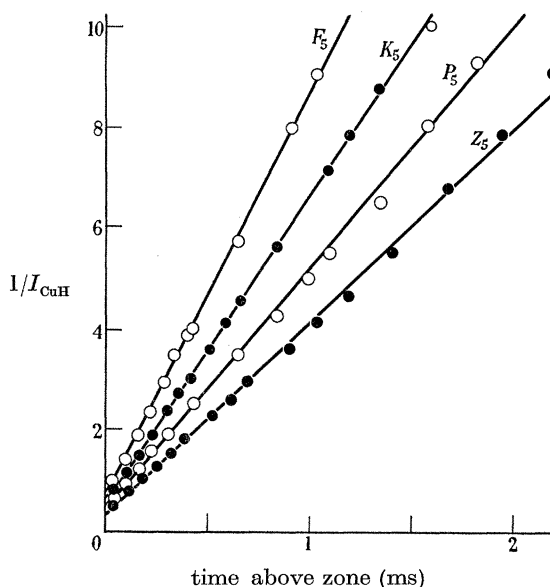

FIGURE 5. Second-order decay of concentration of atomic hydrogen shown by plots of $1/I_{CuH}$ against time, for family 5 ($N_2/O_2 = 5/1$).
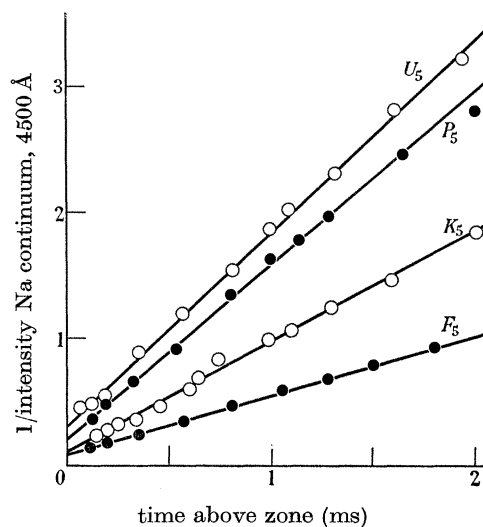

FIGURE 6. Second-order decay of concentration of hydroxyl radicals, shown by plots of $1/$(intensity of sodium continuum) against time, for family 5 ($N_2/O_2 = 5/1$).

4. DISCUSSION

The discussion falls naturally into two sections: one dealing with the high temperature effect, i.e. thermal effects arising from recombination of free radicals, and the other with the low-temperature effect, i.e. chemiluminescence.

Photometric studies (part II) of the sodium and lithium resonance lines, and of the effect of chlorine on the intensity of the sodium D-lines, have shown that the concentrations of H and OH are generally in excess of their equilibrium values, and that where these excesses are sufficiently great the rate of recombination is in accordance with the kinetic laws to be expected from the processes

$$H + H + X \to H_2 + X,$$
$$H + OH + X \to H_2O + X,$$
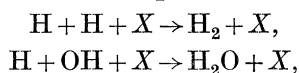
where X is a third body, in this case H_2O, H_2 or N_2—the bulk constituents of the flame gases. Some progress has been made in evaluating the velocity constants of these six reactions (Bulewicz & Sugden 1958), although a complete solution does not appear to be possible in flame gases because of the presence of the balanced reaction $H_2 + OH \rightleftharpoons H_2O + H$.

These assessments were made from observations at heights greater than 1 cm (corresponding to about 1 ms) beyond the reaction zone, and the concentrations of H and OH found there were of the order of 0·1 % of the total gases. Recombination of these amounts of radicals to give equilibrium at, say, 0·01 % would not result in sufficient release of heat to be detectable in the flame gases. However, there is no reason to suppose that the same processes of recombination are not operative nearer to the reaction zone, in which one would expect therefore to find amounts of free radicals up to several parts per cent of the total gases. Recombination in the first centimetre would in this event supply sufficient heat to raise the temperature of the flame gases by 200 to 300 °C, and therefore it would be expected that this would be reflected in the excitation temperature of sodium, granted that thermal equilibrium obtains between sodium and the rest of the flame gases. Gaydon (1957) has discussed the problem of equipartition of energy between translation, rotation and vibration in burnt flame gases, and it may be concluded from his treatment that thermal equilibrium between these degrees of freedom is established after not more than 10^4 collisions, corresponding with a time of about 10^{-5} s or about 10^{-1} mm of height in the flame gases. Little is known about the rate of thermal equilibration between electronically excited atoms and flame gases, but it has been shown that all the alkali elements give the same line-reversal temperatures, based on their resonance lines, in the upper region of the flame gases (part I). These temperatures are reasonable in value, and, it may safely be presumed, represent conditions where such equilibrium has been established. The present observations on flames at high temperatures will now be examined from the viewpoint that such equilibrium occurs up to the reaction zone, the rise in the first millisecond occurring because of heat release from recombination of free radicals. Figures 5 and 6 suggest very strongly that bimolecular recombination (in radicals) is in fact proceeding right up to the reaction zone.

Let R_t be the concentration of free radicals (making no distinction between H and OH, and ignoring others) in moles cm^{-3}, at time t, the temperature being T_t, and let R_0 be the corresponding concentration at any arbitrary starting point in the gases, at which $t = t_0$ and $T = T_0$. If all the heat release between t_0 and t arises from recombination of radicals, one may write

$$mC_p(T_t - T_0) = q(R_0 - R_t), \tag{1}$$

where m = concentration of total burnt gas in moles cm^{-3}, C_p = the average specific (molar) heat of the burnt gas in cal $mole^{-1}$ $°C^{-1}$, and q = average heat released per mole of radicals recombined. If the radicals decay according to a second-order law (in radicals) then

$$\frac{1}{R_t} - \frac{1}{R_0} = kt, \tag{2}$$

the velocity constant k containing the concentrations of third bodies. Hence

$$\frac{1}{(T_t - T_0)} = \frac{mC_p}{kR_0^2 q}\frac{1}{t} + \frac{mC_p}{R_0 q}. \tag{3}$$
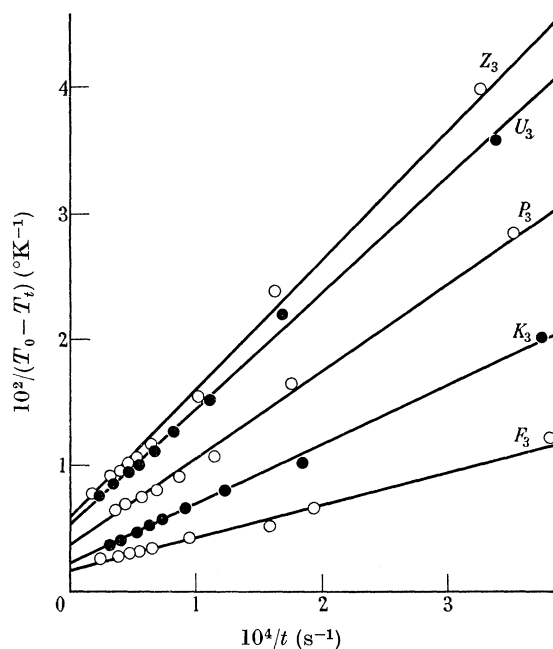

FIGURE 7. Second-order decay of radical concentrations, as estimated from the heat release above the reaction zone. This diagram is a test of equation (3). Flames of family 3 ($N_2/O_2 = 3/1$).

Thus plots of $1/(T_t - T_0)$ against $1/t$ should be straight lines, from whose slopes and intercepts values of R_0 and k should be obtainable. Such plots are in fact quite good straight lines (some examples being shown in figure 7) for observations extending down to rather less than 1 mm above the first visible part of the reaction zone. Table 1 shows the results for k and R_0 deduced from linear plots of this type for several flames in the high-temperature region. In computing this table, m and C_p were estimated for the bulk gas in the region of the final temperature T_f, and q was taken as the mean for $2H \rightarrow H_2$ and $H + OH \rightarrow H_2O$, which have heats of reaction at 298 °K of -104 and -118 kcal $mole^{-1}$, respectively, so that k and R_0 are probably correct to about $\pm 20\%$. T_0 and R_0 refer to points corresponding with about 5×10^{-5} s from leaving the reaction zone, which is probably as near as one may go without questioning the validity of thermal equilibrium.

Bulewicz & Sugden (1958) suggest, from flame photometric measurements of the variation of [H] and [OH] with height in the upper region of the flame gases, that the reaction

$$H + OH + H_2O \rightarrow H_2O + H_2O$$
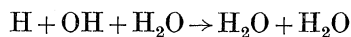
is the dominant one among those possible for recombination in these systems, with a third-order velocity constant at least an order of magnitude greater than that of any of those of the other five reactions involving (H + H) or (H + OH) with the third bodies H_2O, H_2 and N_2. Their estimated values of the third-order velocity constant of this reaction are quoted in table 1 as k'. They compare very well, in general, with $k/[H_2O]$ from the present work. The particular interest of this work is that it provides an essentially thermal method for following the homogeneous combination

TABLE 1

	flame					k (10^{-13} mol.$^{-1}$ cm^3 s^{-1})	$k/[H_2O]$ (10^{-31} mol.$^{-2}$ cm^6 s^{-1})	k' (10^{-31} mol.$^{-2}$ cm^6 s^{-1})
	unburnt composition (volumes)							
symbol	H_2	O_2	N_2	T_f (°K)	R_0 (atm)			
F_3	2·5	1·0	3·0	2460	0·115	1·25	1·2	—
K_3	3·0	1·0	3·0	2360	0·076	1·7	1·7	—
P_3	3·5	1·0	3·0	2270	0·047	2·9	2·7	1·5
U_3	4·0	1·0	3·0	2165	0·032	4·6	4·6	3·3
Z_3	4·5	1·0	3·0	2085	0·029	5·2	5·2	—
F_4	2·5	1·0	4·0	2290	0·076	1·8	1·7	1·8
K_4	3·0	1·0	4·0	2195	0·047	3·8	3·7	3·4
P_4	3·5	1·0	4·0	2110	0·027	5·8	5·7	5·1
F_5	2·5	1·0	5·0	2085	0·057	2·0	2·1	5·3

of free radicals in a flow system. The results are not of sufficient accuracy to allow of a detailed discussion of the variation of velocity constant with temperature, etc. This topic is dealt with more fully by Bulewicz & Sugden (1958), on the basis of more conventional flame photometric data. This agreement between the velocity constants for recombination obtained by entirely different methods, combined with the results of figures 5 and 6, shows that the CuH method for estimating relative [H], and the sodium continuum method for relative [OH] may be used almost up to the reaction zone.

The values of R_0 are of interest in that they can probably be taken, without serious error, as estimates of the order of magnitude of concentration of free radicals in the reaction zone itself. These results show beyond doubt that theories of burning velocity based on considerations of equilibrium concentrations of free radicals, such as that of Tanford & Pease (1947) are not applicable to these flames. A later communication will deal with the correlation of these estimated concentrations of radicals in the reaction zone with the burning velocity.

It is now possible to turn to the low-temperature effect, depicted in figure 2. It is difficult to see what, other than chemiluminescence, could give the very sharp peaks followed by a steady decay of the intensity. At the same time, it is easy to see how such an effect, which would not be expected to vary much with temperature, would be masked by thermal emission from sodium at the higher temperatures, and

indeed the progressive cutting off of the base of the peak with increasing T_f is one of the most striking features of figure 2. It will be supposed that the processes responsible for production of excited atoms Na* are

$$\mathrm{H + H + Na \to H_2 + Na*} \qquad (z_1, q_1),$$

$$\mathrm{H + OH + Na \to H_2O + Na*} \qquad (z_2, q_2),$$
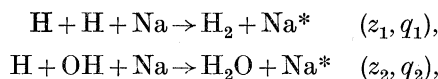
where the z's are collisional factors for the ternary processes and the q's are the probabilities of formation of an excited atom of sodium on collision, and may include both steric and activation factors. The intensity of chemiluminescent emission at any point will then be given by an equation of the form

$$n(1 + \phi\tau) = q_1 z_1 [\mathrm{Na}] [\mathrm{H}]^2 + q_2 z_2 [\mathrm{Na}] [\mathrm{H}] [\mathrm{OH}], \qquad (4)$$

where n is the number of quanta of sodium D-radiation emitted per cubic centimetre per second, and $(1 + \phi\tau)$ is a Stern–Volmer quenching correction in which τ is the mean radiative lifetime of sodium atoms in the excited state, and ϕ is the number of quenching collisions made per second (Mitchell & Zemansky 1934).

This equation is not readily soluble for q, z and ϕ, since the first two of these are, in general, temperature-dependent, and since ϕ will depend on the composition of the burnt gas. It is very desirable, however, to assess its reasonableness from a quantitative standpoint, which may be done by making some simplifying assumptions. The equation (4) may be written

$$n(1 + \phi\tau) = c_1 [\mathrm{H}]^2 + c_2 [\mathrm{H}] [\mathrm{OH}] \qquad (5)$$

for any particular flame, where $c_1 = [\mathrm{Na}] q_1 z_1$, etc., and in which c_1, c_2 may be taken as constant with height, as may also the quenching factor $(1 + \phi\tau)$, since the bulk constituents are likely to provide the major part of the quenching. Because of the rapid balanced reaction $\mathrm{H_2O + H \rightleftharpoons H_2 + OH}$, with equilibrium constant K, the concentrations of H and OH will be related, and one may write

$$n(1 + \phi\tau) = \left(c_1 + c_2 \frac{[\mathrm{H_2O}]}{[\mathrm{H_2}]} K \right) [\mathrm{H}]^2 = c_f [\mathrm{H}]^2. \qquad (6)$$

The decay of H with time may be represented by

$$\frac{1}{[\mathrm{H}]} - \frac{1}{[\mathrm{H_0}]} = \left(k_1 + k_2 \frac{[\mathrm{H_2O}]}{[\mathrm{H_2}]} K \right) t = k_f t, \qquad (7)$$

where k_1 and k_2 are the mean velocity constants for the reactions

$$\mathrm{H + H + X \to H_2 + X,}$$

$$\mathrm{H + OH + X \to H_2O + X,}$$
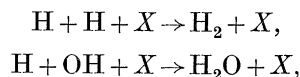
respectively. Combination of equations (6) and (7) yields

$$\frac{1}{\sqrt{n}} = \left(\frac{1 + \phi\tau}{c_f} \right)^{\frac{1}{2}} \left(\frac{1}{[\mathrm{H_0}]} + k_f t \right). \qquad (8)$$

Thus plots of $1/\sqrt{n}$, and hence of $1/\sqrt{I_{\mathrm{Na}}}$, against t should give straight lines if I_{Na}, the intensity of the sodium D-lines in emission, arises predominantly from chemi-

luminescence of this type. Such a plot is shown for a low-temperature flame in figure 8. It is essentially a plot of $1/[H]$ against t if the present interpretation is correct, and it is interesting to note that it is exactly similar to figure 9, which is a plot of $1/[H]$ against time based on the very different CuH type of measurement. This agreement provides the first strong confirmation of the correctness of the chemiluminescence hypothesis.
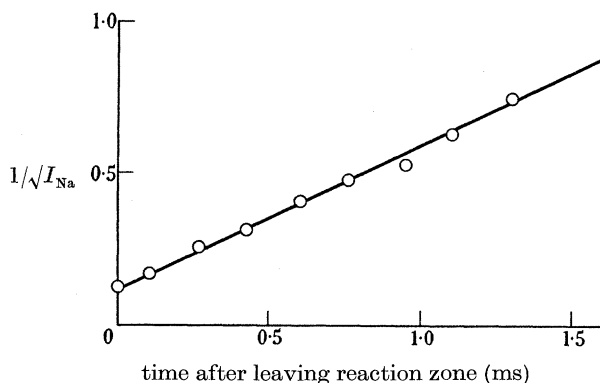

FIGURE 8. The chemiluminescent emission of sodium above the reaction zone for a low-temperature flame, P_8. This diagram is a test of equation (8).
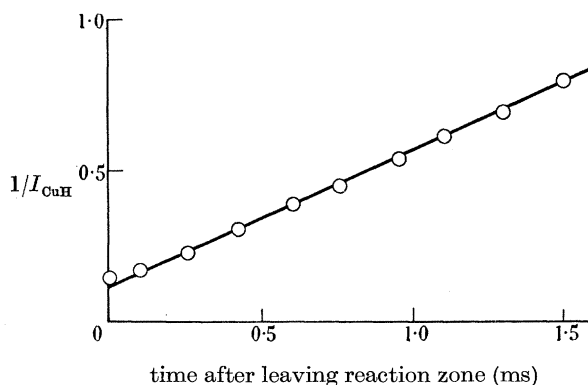

FIGURE 9. The variation of the concentration of atomic hydrogen above the reaction zone, as estimated by I_{CuH}; flame P_8. Compare figure 8.

If the factor of proportionality relating n of equation (8) to I_{Na} is r, then the ratio of the slope to intercept of plots such as that of figure 8 is given by $r^{\frac{1}{2}}k_f$. This factor r may be obtained as follows. n is given by either of the equivalent expressions (Mitchell & Zemansky 1934):

$$n = \frac{8\pi^2 c}{mv^2} Nfl \exp(-hv/kT), \tag{9a}$$

$$n = \frac{Nl}{\tau} \exp(-hv/kT), \tag{9b}$$

where T is the excitation temperature of sodium, f is the 'f-value' for the D-line transition, and l the thickness of the radiating zone. N is the number of sodium atoms per cubic centimetre in the ground state, and may be inferred from a 'van

der Held' curve calibration of the atomizer, in which the concentration of solution which gives a known amount of self-reversal of the D-lines in the flame is observed (part I); in this work 0.001 M sodium chloride gave $N = 8.5 \times 10^{10}$ atoms cm^{-3}. Thus, for a point high up in the flame gases, where T has reached the value T_f corresponding with thermal and chemical equilibrium, n may be calculated, and its ratio to the pointer reading I_{Na} obtained. In the case of the flame of figures 8 and 9 it is then possible to conclude that n at $t = 0$ (the position of peak intensity of the D-lines) is 2.7×10^{12} quanta s^{-1}, for 0.001 M sodium. Hence

$$\left(\frac{1+\phi\tau}{c_f}\right)^{\frac{1}{2}} \frac{1}{[\mathrm{H_0}]} = 6 \times 10^{-7}\,\mathrm{s}^{\frac{1}{2}},$$

$$k_f[\mathrm{H_0}] = 4 \times 10^3\,\mathrm{s}^{-1}.$$

The concentration of atomic hydrogen at $t = 0$, $[\mathrm{H}]_0$, is estimated, from the CuH method combined with the absolute Li–Na resonance line method of part II, to be 5×10^{16} atoms cm^{-3}. This yields

$$\{(1+\phi\tau)/c_f\}^{\frac{1}{2}} = 3 \times 10^{10}\,\mathrm{mol.\ cm}^{-3}\,\mathrm{s}^{\frac{1}{2}},$$

$$k_f = 8 \times 10^{-14}\,\mathrm{mol.}^{-1}\,\mathrm{cm}^3\,\mathrm{s}^{-1}.$$

If $\mathrm{H_2O}$ molecules are the predominant third bodies in bringing about recombination of radicals, their concentration in this flame being about 10^{18} mol. cm^{-3}, then the third-order velocity constant for recombination of radicals becomes 8×10^{-32} mol.$^{-2}$ cm^6 s^{-1} in this flame (P_8). This figure is well within an order of magnitude of those obtained for the hotter flames using the high-temperature effect, and quoted in table 1. Such agreement, bearing in mind all the possible sources of error in the two entirely different methods of assessing the velocity constant, provides good quantitative evidence of the link between the chemiluminescence and the concentration of free radicals.

The quenching factor $(1+\phi\tau)$ is difficult to estimate accurately, on account of lack of knowledge of the number of quenching collisions per second. There appear to be no data for this with respect to $\mathrm{H_2O}$, which would be expected *a priori* to be a powerful quencher. The collision frequency of flame-gas molecules is of the order of 10^9 s^{-1}, so that one might expect between 1 and 10 quenching collisions in the radiative lifetime of sodium, assuming 100 % efficiency of $\mathrm{H_2O}$ in this respect. This would make the factor $(1+\phi\tau)$ take a value of 7 ± 4. This gives $c_f = 8 \times 10^{-21}$ mol.$^{-1}$ cm^3 s^{-1}, and, dividing this by the concentration of atomic sodium in the ground state (8.5×10^{10} atoms cm^{-3}) a value of 1×10^{-31} mol.$^{-2}$ cm^6 s^{-1} for the mean ternary velocity coefficient for excitation of atomic sodium at collisions with either 2H or H + OH. The probable error on this figure is not far short of an order of magnitude, but the figure itself is very reasonable, in that it is of the same order as the ternary velocity coefficients for radical recombination noted above.

The general characteristics of the low-temperature effect having been satisfactorily explained on the basis of the hypothesis of chemiluminescence, a more detailed examination of the reactions involved may be made. Since the range of flames over which the fall in chemiluminescence is not interfered with by rising thermal emission is limited, except in the immediate vicinity of the reaction zone,

attention will be focused on the peak intensity, which will be denoted by $I_{Na(0)}$. This, the intensity in the reaction zone, is plotted against $1/T$ in figure 10, where the lines connect flames of a given 'family' (in which N_2/O_2 is constant in the unburnt gas). Two features may be noted. First, there is a 'family' effect—i.e. the peak intensity is not a smooth function of temperature for all the flames, but shows an isothermal variation, being greater for a given temperature in flames farther from stoicheiometry on the fuel-rich side (in a given family the hotter flames are nearer to stoicheiometry). Secondly, the total variation in peak intensity is rather small.
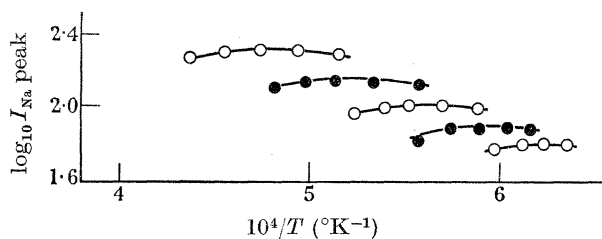

FIGURE 10. The relation of the peak chemiluminescent intensity for Na D-lines in the reaction zone to temperature and composition. Flame families 4, 5, 6, 7 and 8.
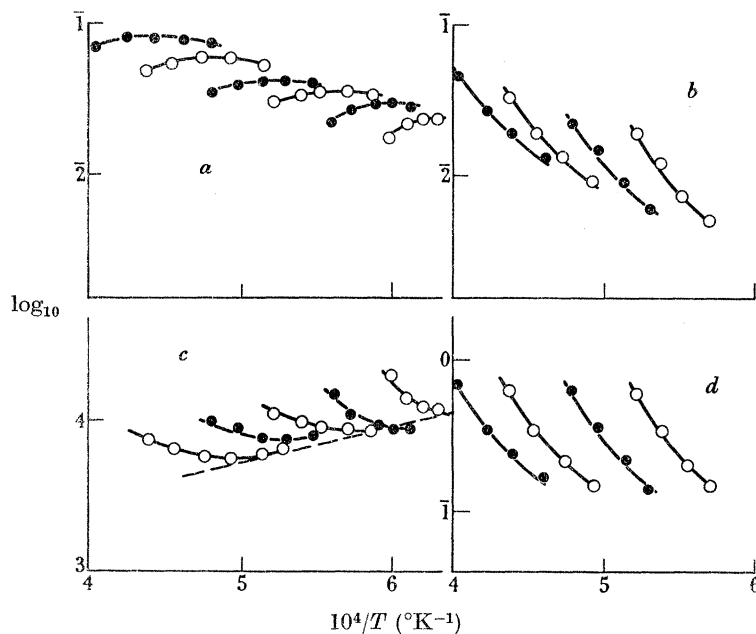

FIGURE 11. Functions of the radical concentrations estimated for the reaction zone. (a) atomic hydrogen $[H]_0$; (b) hydroxyl $[OH]_0$; (c) $I_{Na}/[H]_0^2$; (d) $[OH]_0/[H]_0$.

Equation (8) may be rearranged to give

$$\frac{I_{Na(0)}}{[H]_0^2} = \frac{1}{r}\frac{c_f}{(1+\phi\tau)} \tag{10}$$

at $t = 0$, which is taken to be the point of peak intensity. $[H]_0$, the concentration of atomic hydrogen at this point, may reasonably be obtained by the CuH method, with extrapolation, as explained above. Figure 11 shows plots of $[H]_0$ and $I_{Na(0)}/[H]_0^2$

against $1/T$ for the various families, as well as plots of $[OH]_0$, the concentration of hydroxyl in the reaction zone, obtained from extrapolation of sodium continuum plots such as those of figure 6. The ratio $[OH]_0/[H]_0$ is also given. $I_{Na(0)}/[H]_0^2$ shows an isothermal dependence on composition, which can arise in two ways:

(i) c_f is a function of composition; it may be expanded to give

$$c_f = c_1 + c_2 \frac{[OH]_0}{[H]_0},\tag{11}$$

where c_1 is effectively the velocity constant for excitation of sodium by collision with $H + H$, and c_2 that for excitation by $H + OH$. If the former process operated
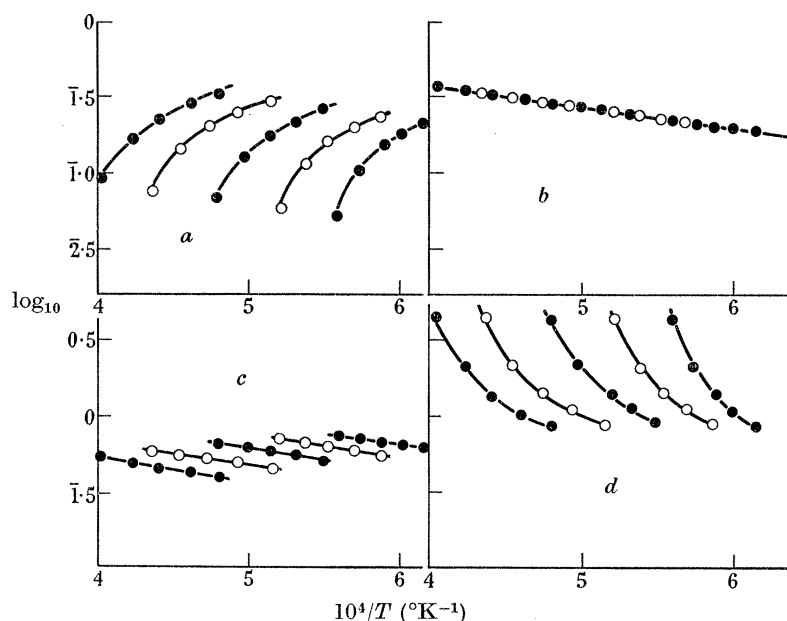

FIGURE 12. Concentrations of the major constituents of the flame gases for the various families are shown in (a) to (c). (a) $[H_2]$; (b) $[H_2O]$; (c) $[N_2]$. Diagram (d) gives $[H_2O]/[H_2]$.

exclusively there would be no composition effect, while the latter would produce an effect equal to that in $[OH]_0/[H]_0$ (figure 11d). The observed variation of $I_{Na(0)}/[H]_0^2$ is intermediate.

(ii) ϕ is a function of composition, since quenching can occur by collision with any of the three bulk constituents H_2O, H_2 and N_2:

$$\phi = g_{H_2O}[H_2O] + g_{H_2}[H_2] + g_{N_2}[N_2],\tag{12}$$

where the g's are proportional to the cross-sections for quenching. The composition of the burnt gas with respect to these constituents is shown in figure 12, together with the ratio $[H_2O]/[H_2]$. Here it may be noted that, (i), $[H_2O]$ is a smooth function of temperature, and (ii), the ratio $[H_2O]/[H_2]$ shows exactly the same composition effect as does $[OH]_0/[H_2]_0$.

There is a good deal of information available about the quenching cross-section for Na* in H_2 and N_2 (Mitchell & Zemansky 1934; Norrish & Smith 1940; Laidler

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1954), but unfortunately none for the case of H_2O, which molecule might be expected to be rather an effective quencher for excited sodium. If it were much more effective as a quencher than either H_2 or N_2, then ϕ would show no effect of varying the composition; in any case, there will be only a small resultant composition effect, since H_2 and N_2 are about equally effective in quenching, and the function $([H_2]+[N_2])$ in the burnt gas must be smooth with temperature. Hence, it seems very reasonable to take ϕ as a smooth function of temperature, and to ascribe the composition effects of $I_{Na(0)}/[H]_0^2$ (see figure 11) to the factor c_f.

If this is the case, it is now possible to combine the data of figures 11a and 11d to obtain values of c_1/c_2. This ratio is found to be 0.4 ± 0.1 over the whole range of temperatures. The dotted line of figure 11c shows the limiting effect for very hydrogen-rich flames, where $c_f \to c_1$, and the excitation is only by

$$Na + H + H \to Na^* + H_2.$$
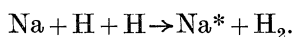
The positive slope of this limiting straight line may arise from either a decrease of c_1 with increasing temperature (i.e. shorter duration of 'sticky collisions'), or from the increasing amount of H_2O in the burnt gas at the higher temperatures, assuming this to be by far the best quencher. In the case of the flame for which results are depicted in figures 8 and 9, for which $c_f = 8 \times 10^{-21} \, \text{mol.}^{-1} \, \text{cm}^3 \, \text{s}^{-1}$, we have therefore

$$c_1 \sim 2 \times 10^{-21} \, \text{mol.}^{-1} \, \text{cm}^3 \, \text{s}^{-1},$$
$$c_2 \sim 5 \times 10^{-21} \, \text{mol.}^{-1} \, \text{cm}^3 \, \text{s}^{-1},$$

and, dividing these by [Na] $(8.5 \times 10^{10} \, \text{mol. cm}^{-3})$ (see (5)),

$$q_1 z_1 \sim 2 \times 10^{-32} \, \text{mol.}^{-2} \, \text{cm}^6 \, \text{s}^{-1},$$
$$q_2 z_2 \sim 6 \times 10^{-32} \, \text{mol.}^{-2} \, \text{cm}^6 \, \text{s}^{-1}.$$

The calculation of the ternary collision frequencies z on the basis of the kinetic theory of gases is a very uncertain matter, and it is probable that the best method is the rather crude one of multiplying the binary collision frequency by the ratio (collision diameter/mean free path). With collision diameters of 3×10^{-8} cm, both z_1 and z_2 fall into the range of 10^{-31} to $10^{-32} \, \text{mol.}^{-2} \, \text{cm}^6 \, \text{s}^{-1}$, making the probability factors q of the order of unity.

These results are obviously not sufficiently accurate to be used as a test of the theoretical work of Magee & Ri (1941) on the $Na + 2H$ reaction, but it is of interest to note that their work predicts an energy of activation of 6.5 kcal/mole for this reaction. This would make about one collision in six effective at 1500 °K, which is not inconsistent with the present work.

In conclusion, therefore, it has proved possible to give an account, in quantitative terms, of the intensity of emission of the sodium D-lines from hydrogen flames over a wide range of temperature. The results are of great interest in view of the light which they throw on the concentrations and rates of recombination of free radicals in burnt flame gases.

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