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# QUARTERLY REVIEWS

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## THE EMISSION SPECTRA OF FLAMES

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THE spectroscopic study of flames is primarily of interest because of the information it gives about the chemical and physical processes occurring during combustion, but it also has a wider interest in that it gives information about such things as the transfer of energy in collisions between excited molecules and the probability of conversion of energy of one form, such as rotational, vibrational, or electronic excitation energy, into other forms. Several of the band spectra emitted by flames, such as those of the radicals HCO, BrO, and IO, are not readily obtained from other sources, and so the study of the appropriate flame spectra serves to give information about the structure of these emitters.

For processes of slow combustion, below the ignition point, it is possible to follow the reaction by chilling and chemical sampling. By studying the effects of diluents and catalysts on the rate of reaction, and the effect of changing the composition of the mixture, the pressure, or the temperature, a great deal of information can be obtained, and by applying the methods of chemical kinetics to the results it is in many cases possible to give a detailed account of the chemical reactions during oxidation. These reactions often involve chain mechanisms maintained by active radicals or even free atoms. For ordinary hot flames, however, chemical sampling is of little avail and very little is known with certainty about the details of reactions in the flame front. Perhaps the most characteristic feature of combustion as opposed to other chemical reactions is the appearance of a visible flame, and it is natural to attempt to use information about the quantity and quality of the light emitted to attempt to find out something about processes occurring in the flame front.

There are many ways in which spectroscopic methods assist in the understanding of combustion. The emission spectrum of the flame primarily tells us about the electronically activated species present in the flame. From their study we learn that many radicals unknown in ordinary chemistry are present in the flame, and from the intensity distribution within the band systems we learn much about the methods by which these radicals are formed, how they acquire energy, and how they lose it. The study of absorption spectra is also a potentially important method, but in practice, although it has given some useful information about slow

combustion, it is found that flames do not absorb appreciably, only the bands of the OH radical being obtained under normal conditions. It is found that the infra-red emission spectrum is characteristic of the vibration-rotation spectra of the molecules which are the final products of the combustion, water vapour and carbon dioxide ; it gives valuable information about the vibrational energy of the product molecules but bands of intermediary compounds are not usually recorded. Spectroscopic data are also used extensively for determining specific heats at high temperatures and energies of dissociation ; these values are required for calculations of flame temperatures and of the extent to which particular reactions may absorb or evolve heat.

This review will be limited to the emission spectra of flames in the visible and ultra-violet and to spectroscopic methods of temperature measurement, with a final discussion on the excitation conditions in flames. For a much fuller discussion of the whole subject of the applications of spectroscopy to combustion problems with a bibliography up to 1946 the reader is referred to the author's monograph.<sup>1</sup> Here, the background to the subject will again be covered, but the emphasis will be on developments in the last few years and the trend of future work.

### Emission Spectra

Spectra in the visible and ultra-violet correspond generally to electronic transitions ; that is, an electron changes from one orbital to another and the energy liberated in the change is emitted as light. The spectra so obtained fall into three types, namely, line, band and continuous. Line spectra are due to transitions between quantised states of free atoms ; they are not usually of great importance in the study of flame spectra, for the atoms which are normally present in the flames of pure gases, those of hydrogen, oxygen, nitrogen, and carbon, require such large energies for their excitation that they are not obtained in flames, except the carbon line at 2478 Å. which is emitted weakly by very hot flames, such as the oxy-acetylene flame ; metallic lines are, of course, more easily excited and may appear either as an impurity (*e.g.*, the Na lines) or if organo-metallic dopes are added (*e.g.*, Pb lines from tetraethyl-lead, or Fe lines from iron carbonyl) ; they are of importance in determining flame temperatures. Band spectra are similarly due to transitions between quantised energy states in molecules ; molecules possess energy of rotation and internal vibration as well as electronic excitation, and since the energy in these forms usually changes at the same time as the electronic transition occurs the spectrum becomes more complex. For each electronic transition, corresponding in the case of an atom to a single spectrum line, there will be a whole band system. In this there are a number of bands each of which corresponds to a particular change of vibrational energy and each band consisting of a large number of closely spaced spectrum lines ; this line structure of the band is due to the rotation of the molecule, each line being due to a different change in the rotational energy. The most characteristic features of flame spectra are band systems,

<sup>1</sup> A. G. Gaydon, "Spectroscopy and Combustion Theory", London, 1948.

and their structure will be discussed a little more fully. The third general type of spectra are continuous and are due to electronic transitions in which one of the states, either the initial or the final state of the system, is unquantised and possesses free kinetic energy; examples are a transition from a stable electronic state of a molecule to an unstable state in which the molecule dissociates spontaneously, or a union of an electron with a positive ion to form a neutral atom, the energy of recombination plus the free kinetic energy of approach being emitted as light. These continuous spectra are therefore due to processes. Flames usually emit a certain amount of continuous radiation, and sometimes give strong continua, and a section will be devoted to this subject.

The simplest band spectra, and fortunately those most often emitted by flames, are due to diatomic molecules. There is a single mode of vibration, and the vibrational frequency is usually slightly different in the excited and the unexcited electronic states. The vibrational energy is quantised and is equal to the product of the vibrational quantum number  $v$  and a number  $\omega$  which is proportional to the vibrational frequency,  $E_v = v\omega$ , or more correctly to a power series in  $v$ , of the form  $E_v = v\omega - v^2x\omega + v^3y\omega + \text{etc.}$ , where the higher terms represent the closing up of the vibrational energy levels towards the dissociation limit. Any band may be denoted by the values of the vibrational quantum number  $v$  in the excited and lower electronic states as the  $(v', v'')$  band. Thus the (3,1) band would be that for which the vibrational quantum number had a value of 3 in the excited electronic state and 1 in the unexcited state. All changes of vibrational quantum number are allowed, but the strength of a band depends on the population in the excited state and on the transition probability which may be derived qualitatively with the aid of the Franck-Condon principle or more accurately from wave mechanics. The lines of the rotational fine structure form series or *branches*. All the lines in a branch have the same change in rotational quantum number; the R branch is due to a decrease of one unit in rotational quantum number, the Q branch to no change, and the P branch to an increase of one unit. From the rotational fine structure of a band it is possible to derive the moment of inertia of the molecule and to learn something about the types of electronic states involved; this information is of value in fixing the emitter of the band system. For the theory of molecular spectra the books by W. Jevons<sup>2</sup> or G. Herzberg<sup>3</sup> may be consulted.

For polyatomic molecules there are more possible modes of vibration and both the vibrational and the rotational structure of the band system are much more complex.

The emission spectrum depends, of course, not only on what molecules are present, but on the amount of excitation energy available in the source. Thus carbon monoxide and nitrogen give strong spectra in discharge tubes but do not give any emission from flames because the electronic energy levels involved require too much energy. Some molecules apparently have

<sup>2</sup> "Report on band spectra of diatomic molecules", The Physical Society, 1932.

<sup>3</sup> "Molecular spectra and molecular structure", Prentice-Hall, 1939.

excited electronic states which are unstable and these cannot give banded emission spectra, although in absorption they may show continuous or diffusely banded systems. Many free radicals and intermediary compounds which one might expect to be present in flames, such as  $\text{HO}_2$ , cannot be detected spectroscopically.

Under equilibrium conditions the strength of any particular band system will be related to the amount of the emitting species present and to the flame temperature. In flames, however, especially in the region of the flame front, there is no equilibrium, and great care is required in using spectroscopic results because the strength with which a band system is emitted will depend not only on the number of excited molecules formed but also on their subsequent reactions. The average time before an electronically excited molecule will radiate is around  $10^{-6}$  to  $10^{-8}$  sec. and since a molecule makes about  $10^{10}$  collisions per second at atmospheric pressure it will on the average make between 100 and 10,000 collisions before it radiates. Clearly, if molecules are formed in excited states by chemical processes (chemiluminescence) the nature of these subsequent collisions will be of great importance in modifying both the intensity and the character of the light emitted, because collisions, besides causing electronic deactivation, may change either the rotational or the vibrational energy.

The experimental study of emission spectra is quite straightforward, the chief difficulty being to obtain sufficient light, since flames are normally relatively weak emitters. Prism instruments are generally to be preferred to gratings and ordinary standard types of small and medium quartz spectrograph are suitable for many purposes, although for weak flames really high-aperture instruments of the type used for Raman spectra are most suitable. For detailed study of rotational fine structure of band systems, as in the determination of effective rotational temperatures, larger dispersion is required and quartz or glass prism instruments of the Littrow type are most suitable. A recent development which is likely to become of importance in the study of transient flames, such as single explosion flames, is the use of photon multiplier tubes with electronic amplification and recording on a cathode ray oscillograph; J. T. Agnew, R. G. Franklin, R. E. Benn, and A. Bazarian<sup>4</sup> describe the use of an image orthicon for this purpose.

### Band Spectra in Flames

**The Hydrogen Flame.**—The flame of clean dust-free gases is usually practically non-luminous in the visible region of the spectrum, but in the near ultra-violet a well-defined band system is obtained. The bands are degraded to longer wave-lengths and the strongest head, of the (0,0) band, is at 3064 Å. The next most outstanding head is that of the (1,0) band at 2811 Å., and the (2,0) and (0,1) band heads at 2608 and 3428 Å. are readily seen on well-exposed plates. The rotational fine structure is relatively open, indicating a small moment of inertia. The regular vibrational structure of the system shows that we are dealing with a diatomic molecule, and the open rotational structure shows that this must be a hydride. Each branch

<sup>4</sup> *J. Opt. Soc. Amer.*, 1949, **39**, 409.

is double, indicating that the electronic states are doublets, or that the molecule has an odd number of electrons. There can be no doubt that the emitter is the hydroxyl radical OH, and this was shown by W. W. Watson<sup>5</sup> and D. Jack,<sup>6</sup> who made a detailed analysis of the spectrum.

This discovery of hydroxyl radicals has had considerable influence on the combustion theory, and it is now generally accepted that the reaction occurs through chain processes in which OH plays an important part.

The chain reactions also involve free atoms of oxygen and hydrogen and the complex HO<sub>2</sub>. We shall see later that there is some indirect spectroscopic evidence for the presence of O and H, but there is no record of any band which could be attributed to HO<sub>2</sub>; this complex is probably relatively stable in the lowest electronic state but the excited electronic states are unstable so that it does not possess a band spectrum.

Although hydrogen-air flames are practically non-luminous, hydrogen-oxygen flames do emit some light in the visible. There is some faint banded structure at the red end which is due to the pure rotation-vibration spectrum of H<sub>2</sub>O (*i.e.*, to change of vibrational and rotational energy only, not electronic), this being an extension of the infra-red emission to shorter wavelengths. It was first reported by T. Kitagawa<sup>7</sup> and studied in more detail by Gaydon,<sup>8</sup> who found the bands strongest in the reddish cap of a diffusion flame of oxygen burning in an atmosphere of hydrogen. The pre-mixed oxy-hydrogen flame is rather bluish and the spectrum appears to be continuous when examined with small dispersion, but may be due at least partly to bands of O<sub>2</sub> since H. G. Wolfhard and Gaydon<sup>9</sup> have recently obtained the Runge emission bands of O<sub>2</sub> weakly in a diffusion flame of oxygen and hydrogen.

**The Carbon Monoxide Flame.**—This bright blue flame shows a strong continuous spectrum in the blue and near ultra-violet with a complex system of narrow diffuse bands superposed on this continuum. These bands have received a good deal of attention (*e.g.*, F. R. Weston,<sup>10</sup> V. Kondratjew,<sup>11</sup> and Gaydon<sup>12</sup>). The complex vibrational structure shows that the bands are due to a polyatomic emitter and it is now generally accepted, although without rigid proof, that this is carbon dioxide. No similar spectrum of this gas can be excited in discharge tubes or other sources (except in the afterglow of carbon dioxide in a discharge tube in which the monoxide and oxygen recombine with a sort of low-pressure flame) and this is a case where the flame spectrum is the only source available. The reason for this may be that the carbon dioxide molecule probably has a rather markedly different shape or size in the excited electronic state from that in the normal state. Thus in absorption the energy for this change has to be added to that for the electronic transition and the absorption spectrum lies far down in the ultra-violet. In emission all the energy

<sup>5</sup> *Astrophys. J.*, 1924, **60**, 145.

<sup>6</sup> *Proc. Roy. Soc.*, 1927, *A*, **115**, 373; 1928, *A*, **118**, 647; *A*, **120**, 222.

<sup>7</sup> *Proc. Imp. Acad. Tokyo*, 1936, **12**, 281.   <sup>8</sup> *Proc. Roy. Soc.*, 1942, *A*, **181**, 197.

<sup>9</sup> *Nature*, 1949, **164**, 22.

<sup>10</sup> *Proc. Roy. Soc.*, 1925, *A*, **109**, 175, 523.

<sup>11</sup> *Z. Physik*, 1930, **63**, 322.

<sup>12</sup> *Proc. Roy. Soc.*, 1940, *A*, **176**, 505.

of the electronic transition is not emitted, some being retained as vibrational energy owing to the change in equilibrium configuration, so that the emission spectrum lies to longer wave-lengths, around the blue. In such cases it seems that excitation by electron impact is inefficient, so that the spectrum is not readily excited by electric discharges, but in flames where the excitation may be due either to chemiluminescence or to conversion of excess vibrational energy into energy of excitation it is possible for the bands to be emitted quite strongly. This idea that the carbon dioxide molecules have a different size or shape in the two states leads to the conclusion that in the combustion of the monoxide the new dioxide molecules may initially possess excess vibrational energy. This may account for certain peculiarities of the combustion of dry carbon monoxide, such as the long after-burning, the latent energy, manifest as a failure to reach the theoretical flame temperature, and the abnormally high amount of dissociation in the flame gases (see Gaydon <sup>1, 13, 14</sup>).

It has been shown by Kondratjew that the light yield is very high for the carbon monoxide flame and increases somewhat at reduced pressure, reaching a value of 1 quantum emitted for every 125 carbon dioxide molecules formed. This is evidence that we are dealing with a chemiluminescence rather than with thermal excitation. It may be noted that a normal carbon dioxide molecule in its  $^1\Sigma$  electronic state cannot be formed from normal  $^1\Sigma$  CO and normal atomic oxygen  $^3P$  because of the spin conservation rule. Hence electronic rearrangement must occur at some stage.

Recently G. A. Hornbeck <sup>15</sup> has observed the Runge bands of  $O_2$  in emission from carbon monoxide explosion flames with  $O_2$ . These bands also occur in stationary flames of carbon monoxide and oxygen, but not with carbon monoxide and air,<sup>9</sup> and although Hornbeck at first appeared inclined to attribute the  $CO_2$  band structure to  $O_2$  it is now clear that the ordinary banded structure of the flame spectrum cannot be identified with  $O_2$  bands and that in flat diffusion flames the two band systems are emitted from different regions of the flame. R. C. Herman, H. S. Hopfield, G. A. Hornbeck, and S. Silverman <sup>16</sup> have also obtained the atmospheric A band of oxygen at 7593 Å. and associated bands in emission from the  $CO-O_2$  explosion flames. This band is due to a forbidden transition,  $^1\Sigma_g^+ - ^3\Sigma_g^-$ , and is usually only obtained in absorption with very long path lengths; its occurrence, definitely shown in the good spectra reproduced in the original paper, is remarkable and clearly indicates again some chemiluminescence. K. J. Laidler <sup>17</sup> has discussed the collisions of electronically excited carbon dioxide molecules with normal oxygen molecules and shown that it may lead to the excitation of  $O_2$  to the upper  $^1\Sigma_g^+$  level of the A band, or to the upper  $^3\Sigma$  level of the Runge bands, although in the latter case an activation energy of around 15 kcals. per mole is required; the excited state of carbon dioxide is probably  $^3II$ .

**Organic Flames.**—Flames of hydrocarbons and related compounds such

<sup>13</sup> *Proc. Roy. Soc.*, 1941, A, **178**, 61.

<sup>15</sup> *J. Chem. Physics*, 1948, **16**, 1005.

<sup>17</sup> *Ibid.*, p. 221.

<sup>14</sup> *Nature*, 1942, **150**, 636.

<sup>16</sup> *Ibid.*, 1949, **17**, 220.

as ethers and the higher alcohols and aldehydes when pre-mixed with air or oxygen give a flame of the Bunsen type. In this the radiation may be considered for convenience as coming from three regions, the inner cone, the interconal gases, and the outer cone. The inner cone corresponds to the reaction zone for the initial reactions of the fuel with oxygen; it is a thin brightly luminous layer, of the order of 0.1 mm. thick and usually roughly conical in shape; it is, spectroscopically, the most interesting region, showing various band systems. The interconal gases just above the inner cone consist of the relatively stable products of the partial combustion in the absence of sufficient oxygen, such as carbon monoxide, and hydrogen mixed with some carbon dioxide and water vapour and various dissociation products; these interconal gases give little radiation, although they do, of course, emit the OH bands. The outer cone consists of a diffusion flame of these partly burnt products reacting with the surrounding air; under normal conditions the emission consists of strong OH bands and the spectrum characteristic of burning carbon monoxide. In a burner of the ordinary Bunsen type it is necessary to study the inner cone with some overlapping from the radiation of the surrounding interconal gases and outer cone. By using a Smithells flame separator it is possible to separate the inner and outer cones; in this the inner cone is maintained on the end of a quartz tube and within another quartz tube of slightly larger diameter, so that the inner cone is only surrounded by the interconal gases which burn as an outer cone at the top of the larger quartz tube.

In addition to the OH bands, three other important band systems are emitted from the inner cone. These are the strong green bands discovered by Swan and now known to be due to  $C_2$ , the strong bands in the blue-violet at 3900 and 4315 Å. which are due to CH, and the hydrocarbon flame bands, a weaker system in the near ultra-violet first studied by W. M. Vaidya.<sup>18</sup> The strengths, both absolute and relative, of these systems vary markedly with the mixture strength and with the nature of the fuel.

Flames of very rich mixtures usually give solid carbon formation and the continuous emission from the white-hot carbon particles masks any more interesting features. The banded emission from a Bunsen flame which is only just luminous at the tip is, however, relatively weak. As the aeration of the flame increases, the inner cone shortens and becomes brighter and the bands of  $C_2$ , CH and OH increase in strength. The  $C_2$  bands reach their maximum well on the rich side of stoichiometric, and die out rapidly for fuel-weak mixtures. The CH bands are also strongest on the rich side of stoichiometric but are best in slightly less rich mixtures than the optimum for  $C_2$ , and the CH bands do not die out so rapidly as we pass to weak mixtures. The OH bands are rather weak in very rich mixtures, reach their maximum strength around the stoichiometric point, and remain fairly strong in weak mixtures. The hydrocarbon flame bands are relatively strongest in weak mixtures. Under some conditions they may extend into the outer cone of the flame, especially if the inner cone is chilled, as in struck-back flames (Gaydon<sup>19</sup>).

<sup>18</sup> *Proc. Roy. Soc.*, 1934, A, **147**, 513.

<sup>19</sup> *Ibid.*, 1942, A, **179**, 435.

The  $C_2$  bands are emitted most strongly by the unsaturated hydrocarbons (acetylene, ethylene, benzene) but also quite well by all hydrocarbons, including methane, and ethers. They are absent from the flame of formaldehyde and only weakly present in a fuel-rich methyl alcohol flame but not in the stoichiometric flame. Alcohols and aldehydes generally give them rather weakly.

The CH bands are also strongest in hydrocarbon flames but are emitted by the methyl alcohol flame and even weakly by formaldehyde, but not apparently by glyoxal or formic acid.

The hydrocarbon flame bands are strongest with ethylene and acetylene, but are emitted by all hydrocarbon flames and indeed to some extent by flames of a great variety of organic compounds (Vaidya<sup>20</sup>). These bands were assigned provisionally to the emitter HCO by Vaidya, and this is confirmed by their observation in the fluorescence of formaldehyde excited by far ultra-violet light by P. J. Dyne and D. W. G. Style,<sup>21</sup> and by later work of Vaidya burning deuterioacetylene to get DCO bands.

In view of the great strength of the  $C_2$  and CH bands it is surprising that room for these radicals has not been found in the chemical reaction schemes for hydrocarbon combustion. We have still a lot to learn about their role in flames. They may be due to the breaking up of large unstable radicals or peroxides. At one time it was suggested by E. C. W. Smith<sup>22</sup> that the formation of solid carbon particles might be due to polymerisation of  $C_2$  radicals, but this now seems unlikely.<sup>1</sup> The hydrocarbon flame bands seem to be associated with the presence of peroxides in the flame.<sup>19</sup> Chain mechanisms for combustion have frequently required either  $CH_2$  or  $CH_3$  radicals. Bands of  $CH_2$  around 4050 Å. are known in the spectra of comets and in discharges through flowing hydrocarbons (Herzberg<sup>22</sup>), but there does not appear to be any sign of the bands in flame spectra. In some low-pressure flames (acetaldehyde, ether) in which CH bands are relatively strong and  $C_2$  weak, Gaydon and Wolfhard<sup>23</sup> have found weak band structure with open rotational structure in the orange-red. This may perhaps be due to  $CH_3$ .

Explosion flames generally give spectra similar to the corresponding stationary flames, but with the more violent explosions there is a tendency for the spectrum to become more continuous, probably because of excitation of the carbon monoxide flame spectrum (always present in after-burning) in the pressure waves associated with the explosion.

**Cool Flames.**—It is well known that ether, the higher hydrocarbons and aldehydes, and some other compounds show the phenomenon known as cool flames. At temperatures well below the ignition point pale blue flames can be made to pass through suitable mixtures of fuel and oxygen, sometimes only at reduced pressure. It was shown by H. J. Emeléus<sup>24</sup> that the spectra of these very weak flames differed from those of ordinary hot flames.

<sup>20</sup> *Proc. Indian Acad. Sci.*, 1935, **2A**, 352; *Proc. Roy. Soc.*, 1941, *A*, **178**, 356.

<sup>21</sup> *Faraday Soc. Discussions*, 1947, **2**, 159.      <sup>22</sup> *Astrophys. J.*, 1942, **96**, 314.

<sup>23</sup> 3rd Symposium on Combustion, Wisconsin, 1948, p. 504.

<sup>24</sup> *J.*, 1925, **127**, 1362.



The spectrum shows bands in the blue to near ultra-violet which are due to formaldehyde. The effect is clearly due to chemiluminescence, and the subject has invoked much discussion (*e.g.*, B. Lewis and G. von Elbe,<sup>25</sup> A. D. Walsh<sup>26</sup>). J. E. C. Topps and D. T. A. Townend<sup>27</sup> have shown that the light yield is very small; in the case of acetaldehyde there is only one quantum of light emitted for every million acetaldehyde molecules consumed, although this corresponds to one in every 125 formaldehyde molecules formed. It is probable that the appearance of the cool flame, although so characteristic of the phenomenon, is only incidental to the main reaction process. The reaction proposed by Lewis and von Elbe in which acetyl radicals are supposed to react, in a side reaction, with oxygen to form excited formaldehyde, CO and OH, seems more plausible than other suggestions of reaction between  $\text{CH}_3$  and  $\text{O}_2$ .

There is one hot flame which shows the typical cool flame spectrum; that is the flame of methyl alcohol which shows the formaldehyde bands faintly as well as CH and OH. In this case the formaldehyde bands appear in low-pressure flames<sup>23</sup> below the other bands. It is suggested that in the methyl alcohol flame atomic oxygen diffusing back reacts with the alcohol to form excited formaldehyde and water vapour.

**Atomic Flames.**—When powerful electric discharges are passed through oxygen or hydrogen at low pressure (around 0.2 mm. Hg) free atoms are formed. If the gases from such a discharge are led into a combustible vapour then a form of diffuse low-pressure flame may be obtained. Atomic flames have not been observed with methane, carbon monoxide, or hydrogen, but quite bright flames are obtained with atomic oxygen and ordinary organic fuels. With atomic hydrogen rather less intense flames are observed, but a definite luminous reaction does occur.

Early work of this type was carried out by Lord Rayleigh, but the main developments are due to K. F. Bonhoeffer and his colleagues. Early papers on the spectra of these atomic flames were written by P. Harteck and U. Kopsch<sup>28</sup> and Bonhoeffer,<sup>29</sup> and a more complete study made by K. H. Geib and W. M. Vaidya.<sup>30</sup> The spectra of the flames with atomic oxygen are closely similar to those of the ordinary flames with molecular oxygen. Generally bands of  $\text{C}_2$ , CH, OH and HCO are obtained. For methyl alcohol the formaldehyde bands (cool-flame type spectrum) are again obtained in addition to strong OH and weak CH. The results are of interest as showing that atomic oxygen will initiate reaction even at room temperature, but the main reactions even in these atomic flames may still be between undecomposed molecular oxygen and fuel, so that it is necessary to be careful before drawing the obvious conclusion that the luminescence is due to reactions involving oxygen atoms.

The flames with atomic hydrogen show only the band systems of  $\text{C}_2$  and CH. It is generally considered that stripping of hydrogen atoms to

<sup>25</sup> "Combustion Flames and Explosions of Gases", Cambridge, 1928.

<sup>26</sup> *Trans. Faraday Soc.*, 1946, **42**, 269.

<sup>27</sup> *Ibid.*, p. 345.

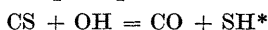
<sup>28</sup> *Z. physikal. Chem.*, 1928, *B*, **12**, 327.

<sup>29</sup> *Z. Elektrochem.*, 1936, **42**, 449.

<sup>30</sup> *Proc. Roy. Soc.*, 1941, *A*, **178**, 351.

combine with H to form molecular hydrogen is the main reaction, successive stripping perhaps leading to  $C_2$  and radicals from which CH breaks off. It seems possible to the Reviewer, however, that the hydrocarbon acts as third body in the recombination of two hydrogen atoms and receives the bulk of the 103 kcals. per mole liberated, this heating of the hydrocarbon leading to decomposition in some cases. The polymerisation reactions which occur in hot flames and in electric discharges through hydrocarbons do not seem to occur appreciably in the atomic flames.

**Inorganic Radicals in Flames.**—Although the study of the spectra of inorganic flames has not contributed so much to the knowledge of their combustion processes, some interesting band systems are observed. Flames of organic compounds containing nitrogen show strong band systems of CN, NH and NO; the same systems are also given by most flames of organic compounds supported by nitrous oxide instead of oxygen. The flame of ammonia burning with oxygen and the hydrogen-nitrous oxide flame also show a complex structure of many lines in the yellow-green known as the ammonia  $\alpha$  band; the emitter is believed to be  $NH_2$ .<sup>31, 1</sup> Flames containing sulphur compounds may also show bands of  $S_2$  and of the radicals SO and CS. The band of SH at 3236 A. is also emitted when sulphur dioxide or hydrogen sulphide is added to organic flames (Gaydon and Whittingham<sup>32</sup>) but not when they are added to a hydrogen flame; this is the only known source of this band in emission, although it was previously known in absorption; there appears to be some form of chemiluminescence involving a carbon compound, such as perhaps



Flames containing phosphorus show bands of PO<sup>33, 34</sup>, but there does not appear to be any record of the PH band in flames, although this is well known in discharge tubes.

Halogens have a well-known inhibitory action on some flames. Most alkyl halides have a marked effect in reducing flame velocities, and some, such as methyl bromide, are used as fire extinguishers. The mechanism is not understood, but interest in the subject has led to the study of flame spectra of these alkyl halides and to the effect of adding halogens to flames. Vaidya has discovered new band systems of IO and BrO in flames of methyl iodide<sup>35</sup> and ethyl bromide.<sup>36</sup> These spectra have recently been studied in greater detail by E. H. Coleman and Gaydon<sup>37</sup> and by Coleman, Gaydon, and Vaidya.<sup>38</sup> A corresponding system of ClO has also been observed by G. Pannetier and Gaydon.<sup>39</sup> Flames containing methyl chloride, chloroform or carbon tetrachloride were also found by Vaidya to show a band system due to CCl; the corresponding systems of CBr and CI are not known.

<sup>31</sup> A. Fowler and J. S. Badami, *Proc. Roy. Soc.*, 1931, A, **133**, 325.

<sup>32</sup> *Ibid.*, 1947, A, **189**, 313.

<sup>33</sup> H. J. Emel us and W. E. Downey, *J.*, 1924, **125**, 2491.

<sup>34</sup> H. J. Emel us and E. H. Purcell, *J.*, 1927, 788.

<sup>35</sup> *Proc. Indian Acad. Sci.*, 1937, **6A**, 122.

<sup>36</sup> *Ibid.*, 1938, **7A**, 321.

<sup>37</sup> *Faraday Soc. Discussions*, 1947, **2**, 166.

<sup>38</sup> *Nature*, 1948, **162**, 108.

<sup>39</sup> *Ibid.*, **161**, 242.

Although as yet there is no sure interpretation of the action of halogens in inhibiting combustion, yet the discovery of the presence of these radicals may have some influence. It is noteworthy that ClO, BrO and IO have not been obtained from any other source as yet. Certain bands of iodine and bromine are also obtained in emission in flames more readily than in other sources.<sup>37, 38</sup>

### Continuous Spectra

It has been pointed out that line spectra and band spectra are due to electronic transitions between two quantised energy states in an atom or molecule, and that continuous spectra are due to processes in which a molecule is formed or dissociated or an atom is ionised or two ions recombine. Nearly all flame spectra show a faint continuous background, and this is

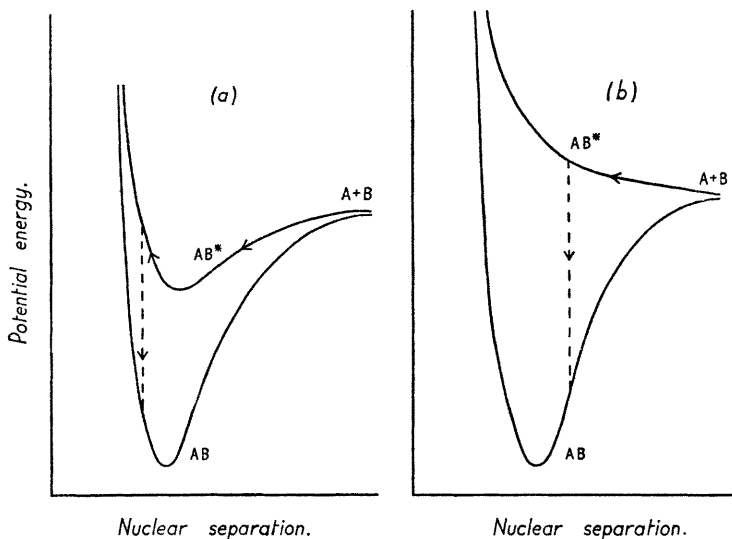


FIG. 1

apparently due to recombination of positive ions and free electrons; although pure flames should not be highly ionised because of the high ionisation potentials of the gas products  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ , etc., yet in practice sufficient impurities such as sodium and calcium seem to be present to produce considerable ionisation.

In chemical kinetics, processes of bimolecular association are usually ruled out because of the difficulty of getting rid of the excess energy. However, in special cases it may be possible for an electronic transition to occur during the short duration of a collision and for the energy of this transition to be radiated, thus stabilising the system. This is illustrated in Fig. 1. Suppose two atoms, A and B, can unite to form either a normal molecule AB or an electronically excited molecule  $\text{AB}^*$ . We assume that the ground state of AB is stable and has the usual form of potential-energy curve with

a pronounced minimum. The excited state may be either stable (Fig. 1*a*) or of the repulsive type (Fig. 1*b*). In the first case it will be possible for two atoms to collide with low energy of approach (*i.e.*, in cold gas) momentarily to form the molecule  $AB^*$  and then during the collision, before the complex decomposes, to radiate and form a stable molecule  $AB$ . In the second case, when  $AB^*$  is repulsive, the duration of the collision in which  $AB^*$  is momentarily formed will be very short and the internuclear separation between A and B will remain large unless the atoms approach with considerable energy (hot gases). Thus the association process cannot occur in cool gases but for hot gases there is again a small chance that light will be emitted and a molecule formed.

The duration of a collision is of the order  $10^{-12}$  to  $10^{-13}$  sec., and the normal radiative life for a fully allowed electronic transition around  $10^{-7}$  to  $10^{-8}$  sec., so that at best the probability of the association taking place is around one in  $10^5$  and may be much less. We can see classically, by the Franck-Condon principle, that in the first case the best chance for radiation will be when the nuclei are at the turning point, so that the transition will be as indicated by the broken line in Fig. 1*a*. We may thus expect a continuous emission with a fairly pronounced maximum of intensity, and the character of the continuum will not be very sensitive to temperature effects. In the second case, illustrated in Fig. 1*b*, however, the continuum is likely to spread over a greater region of the spectrum and both its absolute strength and the position of maximum intensity may change with temperature.

Although the observation of continuous spectra would be expected to give valuable information about the processes occurring in flames, in practice the characteristic lack of measurable features in a continuum makes it difficult to identify continua with definite processes with certainty. Also, most observed continua are not due to the simple association of two atoms visualised above, but to more complex associations in which an atom and a molecule are involved; we then have to deal with complex potential surfaces.

The strong continuous spectrum which is the main feature of the carbon monoxide flame spectrum is believed to be due to reaction of the monoxide and atomic oxygen (Gaydon <sup>40</sup>); it is known that carbon monoxide does not give an atomic flame with oxygen, and hence we may assume that the reaction is as illustrated in Fig. 1*b*; this would account for the preponderance of the continuum over the banded  $CO_2$  emission in hot flames, while cooler flames [with air, at reduced pressure, or the pre-ignition glow (Gaydon <sup>41</sup>)] show less continuum.

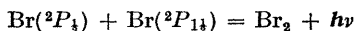
An important continuum is that due to reaction of atomic oxygen with nitric oxide. It is responsible for the afterglow of air in a discharge tube, and has been identified with certainty by M. L. Spealman and W. H. Rodebush.<sup>41</sup> It has maximum intensity in the yellow-green and imparts a yellowish or greenish-yellow colour. An ordinary oxy-hydrogen blowpipe flame running in air usually shows a yellowish tip due to this reaction, and some flames supported by nitrous oxide are strongly coloured by it.

<sup>40</sup> *Trans. Faraday Soc.*, 1946, **42**, 292    <sup>41</sup> *J. Amer. Chem. Soc.*, 1935, **57**, 1474.

Gaydon <sup>40</sup>, <sup>42</sup> has developed a test for the presence of atomic oxygen in flames using this continuum. A small amount of nitric oxide is added to the flame gases and the yellow coloration serves as a qualitative test for atomic oxygen. In hot flames there are always some free oxygen atoms present because of the equilibrium dissociation of the flame gases, but in some flames, particularly that of carbon monoxide, the coloration is very strong and it suggests that oxygen atoms are produced more quickly by the combustion reactions than they are consumed. Hydrogen flames show the presence of some, but not a lot, of oxygen atoms. Hydrocarbon flames show these atoms in the outer cone, but not in the inner cone. The absence of oxygen atoms during the initial reaction processes may be used as an argument against reaction processes, such as modifications of the hydroxylation theory, which require chain mechanism involving atomic oxygen.

Flames containing oxides of sulphur show a strong broad region of continuous emission throughout the blue, violet and near ultra-violet ; <sup>32</sup> it seems that this continuum is due to a reaction of atomic oxygen, but it is not certain whether it is due to  $\text{SO} + \text{O} = \text{SO}_2 + h\nu$  or to  $\text{SO}_2 + \text{O} = \text{SO}_3 + h\nu$ .

Strong continua in the visible and near ultra-violet are also emitted by flames containing halogens, and especially by flames of halogens reacting with hydrogen. H. C. Urey and J. R. Bates <sup>43</sup> have examined the intensity distribution within these continua and have concluded that they are due to reaction of normal with excited halogen atoms to form halogen molecules ; *e.g.*, for bromine,



Reaction between halogen atoms and hydrogen atoms might also give continuous emission, but the observed intensity distribution agrees better with that between halogen atoms as indicated.

### Detailed Study of Reactions in Flame Fronts

Spectroscopic studies of flames are most important when applied to the reaction zone or flame front, because it is in this region that the important and rapid combustion processes are occurring, and it is in this region that chemical sampling cannot be applied. In ordinary Bunsen-type flames the highly luminous reaction zone of the inner cone is very thin (less than 0.1 mm.) and conical in form. Hence, in studying either the emission or the absorption spectrum we have to take at one time light from the whole of the reaction zone, together with some of the radiation and absorption due to the surrounding hot burnt gases. An important recent development due to H. G. Wolfhard is the use of flames of pre-mixed gases burning at very low pressure. The type of burner is shown in Fig. 2. By using very large burner diameters (up to 5½ cm.) and very high pumping speeds it is found that flames may be maintained down to pressures as low as  $\frac{1}{5000}$  atm. and that, with suitable flows, flat disc-shaped flames are obtained with a relatively very thick reaction zone, from a few mm. to 2 or 3 cm. thick.

<sup>42</sup> *Proc. Roy. Soc.*, 1944, *A*, **183**, 111.

<sup>43</sup> *Physical Rev.*, 1929, **34**, 1541.

The combustion processes appear to be essentially similar at low pressure, and for these flames detailed study of the absorption and emission spectra of the various layers of the reaction zone is possible. It is also possible to study the energy distribution by measuring excitation temperatures and effective rotational temperatures.

Flames of hydrocarbons under these conditions are greenish at the base and around the edges and rather blue-violet towards the upper part of the reaction zone. Spectroscopic studies (Gaydon and Wolfhard<sup>44, 45, 46</sup>) show  $C_2$  bands in the base and centre, CH bands in the centre and upper part, and OH throughout the reaction zone. The HCO bands are strongest

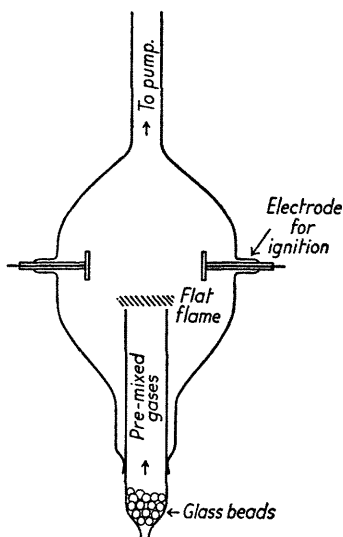


FIG. 2

Burner for low-pressure flames.

rather low in the flame. Under certain conditions in very rich mixtures, however, the CH bands may appear very weakly at the base of the reaction zone, below  $C_2$ . In the methyl alcohol flame, bands of formaldehyde (cool-flame spectrum) are emitted from the very base of the flame, well below the OH, CH and weak  $C_2$  bands. In flames maintained by nitrous oxide,  $C_2$  bands are strongest towards the base, OH and NH extend through the zone, and bands of CH, CN and  $NH_2$  (ammonia  $\alpha$ -band) are strongest higher up. This is the usual order, but in some flames there may be some variation; for example, in ethylene oxide and in methyl alcohol flames the  $NH_2$  bands occur low in the reaction zone.

The only bands which appear readily in absorption in these low-pressure flames are the OH bands, which are detectable with large dispersion provided the pressure be not too low. An interesting feature is that they

can be detected slightly below the luminous reaction zone. It was not clear whether this was due to their diffusing back through the flame against the gas stream or to their formation in pre-flame reactions. Calculations on the distance which radicals and hydrogen atoms could diffuse led to interesting relationships between this distance and the thickness of the reaction zone, and suggested that diffusion is very important in the propagation of flames under these conditions (Gaydon and Wolfhard<sup>47</sup>).

A rather similar development towards the detailed study of the reaction zone of diffusion flames has been made by W. G. Parker and Wolfhard.<sup>48</sup> The principle of the burner is shown in Fig. 3. The fuel and oxygen (or air) flow side by side up rectangular burners, and a surrounding flow of

<sup>44</sup> *Faraday Soc. Discussions*, 1947, 2, 161.

<sup>45</sup> *Proc. Roy. Soc.*, 1948, A, 194, 169.

<sup>46</sup> 3rd Symposium on Combustion, Wisconsin, 1948, p. 504.

<sup>47</sup> *Proc. Roy. Soc.*, 1949, A, 196, 105.

<sup>48</sup> *Proc. Physical Soc.*, in the press.

inert gas (nitrogen) prevents any combustion in the surrounding air. The gas flows are maintained at the same velocity to prevent turbulence. The absorption and emission spectra of the flat diffusion flame can then be studied in detail. With hydrocarbons, carbon formation occurs on the fuel side, with weak  $C_2$  bands slightly towards the oxygen, and CH bands more towards the oxygen. The strong OH bands come next, with their maximum strength well to the oxygen side of the  $C_2$  and CH, although these OH bands extend throughout the flame. Right over on the oxygen side, weak bands of the Schumann-Runge system of  $O_2$  can be detected in absorption and emission.

Recently, J. Powling and Sir Alfred Egerton<sup>49</sup> have developed a flat flame at atmospheric pressure for measurement of flame velocities of gas mixtures near limiting mixture conditions. Owing to the small reaction velocity under these limiting conditions the reaction zone is again relatively thick (up to a few mm.) and in some cases a pre-ignition zone giving a type of cool flame is observed. These flat flames may prove suitable for spectroscopic study.

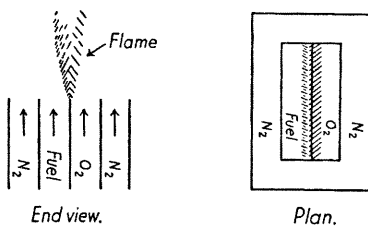


FIG. 3  
*Flat diffusion flame.*

### Temperature Measurements

In a flame front, where energy is being released at a high rate, we cannot expect equipartition of energy among its various possible forms. The energy released in the combustion process may be distributed as kinetic energy of the atoms and molecules (*i.e.*, translational energy), as rotational energy of molecules, as vibrational energy of molecules, as electronic excitation of atoms and molecules, as ionisation, and as chemical energy (as dissociation to free atoms or radicals or any change in equilibrium which will release or absorb energy as the gases cool and reach equilibrium). Clearly, until equilibrium is attained we cannot define the temperature of the reacting gases as a whole, although we may in suitable cases be able to define an effective temperature to express the energy in some particular degree of freedom for some particular atomic or molecular species.

Above the reaction zone of a flame some approach to equilibrium is quickly established and we may attempt to determine the gas temperature. There must always remain the possibility that equilibrium is not perfect, though. It seems that the internal energy of atoms and molecules will reach equilibrium with the translational energy in a reasonably short time, but processes of association of ions to form neutral atoms or molecules, and of association of free atoms to form molecules, require three-body collisions to dissipate the energy of association, and hence these processes may be delayed. It is not unlikely that free atoms of hydrogen and oxygen may persist above the equilibrium concentration for some little while. However, in the interconal gases between the inner and the outer cones of a

<sup>49</sup> J. Powling, *Fuel*, 1949, **28**, 25.

Bunsen-type flame the approach to equilibrium is sufficient to justify an attempt to evaluate the temperature. Resistance thermometry or thermocouples may be used, but are subject to two limitations: first, it is only possible to measure temperatures up to the melting points of the metals used, which in practice usually sets a limit at the melting point of platinum at 1773° c., and secondly, such metals are very sensitive to any lack of chemical equilibrium, and catalytic effects at the surface may give serious error; thus W. T. David, A. S. Leah, and B. Pugh<sup>50</sup> have found a big difference, amounting sometimes to several hundred degrees, between the temperatures given by bare platinum wires and similar wires protected from catalytic effects by a thin film of fused quartz. Thus there are many advantages in determining flame temperatures spectroscopically, and indeed this is practically the only method for very hot flames.

The best and most common method is by spectrum-line reversal. A suitable substance, usually sodium, is introduced into the flame and the spectrum is examined against a background from a hot solid giving a continuous spectrum [for details see E. Griffiths and J. H. Awbery,<sup>51</sup> or refs. (1) or (25)]. If the flame is hotter than the background source (or more correctly than the brightness temperature of the background at that wavelength) the sodium lines are visible in emission, being brighter than the background. If the flame is cooler, then the sodium lines are seen in absorption as dark lines. When the flame and background are at the same temperature then the sodium lines are invisible. This is a simple and reasonably reliable method of measuring the temperature of interconal gases. It may be limited in some cases. There must be a tendency in most flames for the sodium absorption in the cooler outer zones to reduce the observed temperature. A critical examination of this effect, by studying the contours of the sodium lines with an interferometer, has been made by H. M. Strong, F. P. Bundy, and D. A. Larson.<sup>52</sup> Another effect is that, in pre-mixed flames with rich mixtures, there will be a further rise in temperature at the outer cone, and if the sodium vapour reaches this outer reaction zone then the temperature observed will be nearer to the temperature of this outer region than to that of the interconal gases.

The spectrum-line reversal method really gives a measure of the proportion of atoms (of, *e.g.*, Na) which are electronically excited: that is, it gives the "electronic excitation temperature" of the flame. For the interconal gases this coincides quite well with the gas temperature, but in the reaction zone it often comes very much higher.

In luminous flames (*i.e.*, when there is carbon formation) the flame temperature may be deduced from the colour temperature of the flame. It can be shown that the heat transfer to very small particles is very efficient so that the particles will take up the temperature of the flame gases within a very few degrees, despite surface reaction and radiation loss. There is, however, the possibility, as recently stressed by Wolfhard and

<sup>50</sup> *Phil. Mag.*, 1941, **31**, 156.

<sup>51</sup> *Proc. Roy. Soc.*, 1929, *A*, **123**, 401.

<sup>52</sup> 3rd Symposium on Combustion, Wisconsin, 1948, p. 641.



Parker,<sup>53</sup> that particles smaller than the wave-length of light may not behave as black bodies ; carbon particles in flames are believed to be around 500 Å. in size, that is only a tenth of a wave-length.

It is possible to determine the effective rotational temperatures in flame gases for some diatomic molecules. If the spectrum is examined with large dispersion, so that the rotational fine structure is well resolved, the relative intensities of the lines may be measured. Now the intensity of a single line of the rotational fine structure is given by

$$I = CP\nu^4 e^{-E_r/kT}$$

where  $I$  is the intensity,  $C$  is a constant depending on the total intensity, which is the same for all lines,  $P$  is the transition probability for the particular line,  $\nu$  is the wave-number of the line,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $E_r$  is the rotational energy of the upper state for the particular line. The transition probability  $P$  may be evaluated theoretically, and  $E_r$  is obtained from the rotational analysis of the band spectrum. If the logarithm of the observed intensity of the lines minus  $\log(P\nu^4)$  is plotted against  $E_r$ , then a straight line should be obtained from the slope of which  $T$  may be calculated. The line will only be straight if there is a Maxwell-Boltzmann distribution of rotational energy among the molecules, and only when the line is reasonably straight can we assign an effective rotational temperature.

For interconal gases, the only band which is emitted is the OH band, and this usually suffers from the disadvantage that the results are modified by self-absorption, so that this method is of little value for determining true gas temperatures. In the reaction zones of flames, however, besides OH, we have bands of C<sub>2</sub> and CH which are suitable for study, and these give us information about the state of excitation of these molecules. Results by Gaydon and Wolfhard<sup>45, 46, 54, 55</sup> show that for OH the effective rotational temperature in hydrocarbon flames is around 5700° K. at atmospheric pressure, and rises still higher at very low pressure. For some other flames (methyl alcohol, formaldehyde, hydrogen, moist carbon monoxide) the rotational temperature is close to the theoretical flame temperature. For CH the rotational temperature is not very different from the expected flame temperature. For C<sub>2</sub> the rotational temperature is again high, being near 5000° K. for an oxy-acetylene flame at 1 atm., but falling at low pressure.

Attempts have also been made<sup>54</sup> to determine the effective translational temperatures by measuring the Doppler broadening of spectrum lines. In a hot gas the random thermal motion of emitting molecules causes the spectrum line to be displaced either to the red or to the violet according to whether the molecule is moving away from the observer or towards him. Averaged over a number of molecules this results in a broadening of the line. The line breadth due to this cause varies as the square root of the temperature, so the method is not very sensitive. The method used was to cross a Fabry-Perot interferometer with a large quartz Littrow-type spectro-

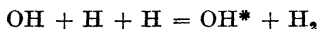
<sup>53</sup> *Nature*, 1948, **162**, 259.

<sup>54</sup> *Proc. Roy. Soc.*, 1949, *A*, **199**, 89.

<sup>55</sup> *Ibid.* 1950, *A*, in the press.

graph. Calculation of results was complicated by need to allow for the finite resolving power of the interferometer. At atmospheric pressure the pressure-broadening of the spectrum lines causes trouble, but some results were obtained at low pressure. For CH surprisingly high translational temperatures, around  $4000^{\circ}$  K., were obtained for the reaction zones of hydrocarbon flames. For OH results were inconsistent because of self-absorption. Unpublished results for lead and iron lines gave about the expected flame temperatures, although the accuracy was not high because of hyperfine structure of the spectrum lines.

It should be possible to learn something about the amount of vibrational energy possessed by the molecules, either by study of the visible and ultra-violet spectrum or by work in the infra-red. So far little work of value has been done on the vibrational intensity distribution in band systems in flames. In low-pressure flames of hydrogen there is abnormal excitation to the  $v' = 2$  level, especially at the top of the flame; this may be due to OH receiving energy as third body in the recombination of free atoms, possible free hydrogen atoms:



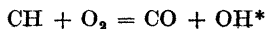
The energy required to excite to  $v' = 2$  is 108.5 kcal. per mole; the above reaction sets free only 103.2 kcal. but the remainder may come from activation energy, being supplied by the heat of the flame.

### Excitation Processes in Flames

Everyone is familiar with the fact that in clear flames of the Bunsen type most of the visible radiation comes from the well-defined inner cone. This luminous layer is only of the order of 0.1 mm. thick and corresponds to the flame front or reaction zone. Why is it that the radiation from this thin zone is so much greater than from the rest of the flame?

To some extent the reason is no doubt that the radicals such as  $\text{C}_2$  and CH which possess band systems favourably situated in the visible region of the spectrum are only present as unstable intermediaries in this region. This is not, however, the whole explanation. The OH bands are emitted much more strongly from the inner cones of organic flames than from the interconal gases where the radicals are still present. The  $\text{C}_2$  and CH bands have not been observed in absorption in flame gases, even by sensitive self-reversal methods, so their concentration must be very small, and yet they radiate so strongly.

A considerable part of the radiation from flames is no doubt due to chemiluminescence, that is the emitting radicals are formed in the excited electronic state by chemical processes. This is certainly true for the formaldehyde emission in cool flames. The high light yield proves the existence of chemiluminescence in the carbon monoxide flame. For hydrocarbon flames the very strong OH emission is best explained by chemiluminescence, as this fits in satisfactorily with the observed high effective rotational temperature and its increase at reduced pressure. In this case the reaction may be



The high electronic excitation temperatures in the reaction zones<sup>45</sup> of flames and the observations on the effective rotational temperature from  $C_2$  bands, especially its fall with pressure or with nitrogen dilution,<sup>55</sup> are not so easily explained as due to chemiluminescence. There is also evidence (H. F. Calcote<sup>56</sup>) that the ionisation in the flame front is higher than it should be on theoretical calculations. To some extent we should expect that before equilibrium is established we should have too few particles of average energy and too many with too little and too much energy, and since it is the very high-energy ones which cause electronic excitation and ionisation, we might expect somewhat more radiation and ionisation than for an equilibrium gas mixture of the same chemical composition. The effect seems, however, too marked for this explanation.

What are the actual collision processes responsible for the electronic excitation of atoms and molecules? The transfer of a relatively light electron from one orbit to another by collision with a relatively massive atom or molecule is unlikely; in fact, it is known that the reverse effect, the quenching of fluorescence by monatomic gases, is most inefficient. The number of free electrons in flame gases may, owing to the abnormally high ionisation, be as much as  $10^{12}$  electrons per c.c., but even so is hardly sufficient (less than 1 in  $10^7$  of the number of molecules) to account for the strong radiation, as we could not expect many of them to possess the necessary high kinetic energy for excitation as well. We are left with three possible explanations: that the active particles possess either electronic excitation energy or excess vibrational energy, or that they are free atoms or radicals liberating energy of recombination to third bodies.

Of these, it seems to the Reviewer most reasonable to assume that the active particles possess excess vibrational energy. It is known that polyatomic molecules with many degrees of vibrational freedom are very good at quenching fluorescence, *i.e.*, that electronic energy of the fluorescent atom is converted into internal vibrational energy of the polyatomic molecule. Presumably, the reverse process could occur and a molecule possessing high vibrational energy could cause electronic excitation. On the other hand, it is also known from studies of supersonic dispersion that excess vibrational energy is not quickly dissipated by conversion into translational energy. During flame reactions it is likely that collision-complexes are formed, perhaps complexes between hydrocarbons or hydrocarbon fragments and oxygen (*i.e.*, peroxides), and that these collision complexes, while inherently unstable and liable to spontaneous decomposition, may distribute the excess energy of their formation among various vibrations and have a reasonably long life and so a chance of giving up this energy to a third body on collision. Clearly, there are many unsolved problems connected with the excitation processes in flames, but detailed study by spectroscopic means of various flames may help in time to solve these problems.

<sup>56</sup> 3rd Symposium on Combustion, Wisconsin, 1948, p. 245.