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CHEMILUMINESCENCE OF FLAMES

[Following is the translation of an article by V. Kondrat'yev entitled "Khemilyuminestsentsiya Plamen" (English version above) in Uspekhi Khimii (Advances in Chemistry), Vol. 12, No. 4, 1943, Moscow, pages 308-317.]

In contrast to thermoluminescence, the source of which is the thermal energy of molecules, chemiluminescence represents a type of emission whose emission is directly related to the energy given off as a result of various elementary chemical processes. Hence chemiluminescence is basically similar to fluorescence, and the luminescence of rarefied gases in an electric discharge appears to be a nonequilibrium emission, i.e. an emission whose intensity is determined by a non-Boltzmann distribution of the energy of excitation.

At one time there was an inclination to ascribe a purely thermal origin to the luminescence of flames. However, with the discovery of rarefied flames it was revealed that in the case of a large number of flames the emission proves to be completely unrelated to the temperature of the flame. All the presently known data pertaining to the emission of flames leads to the conclusion that the emission of most flames represents to a greater or lesser degree pure chemiluminescence.

The problem of the nature of luminescence is resolved with the aid of definite physical criteria, based on the characteristics of chemiluminescence as a nonequilibrium emission. One of the most important criteria of this type is the criterion of absolute intensity of emission. When the absolute intensity of the emission, on the one hand, and the temperature of the flame, on the other hand, are measured, in a number of cases it is possible to ascertain through a comparison of the measured intensity and that calculated from a Boltzmann distribution that the measured intensity exceeds the intensity of equilibrium emission by many orders of magnitude, and that this emission thus represents practically pure chemiluminescence. Such is the case, for example, in the emission of the rarefied flames of CO, H_2, and CS_2, which burn at pressures of several tens of millimeters of mercury. Indeed, measurements of the absolute intensity of the emission in the case of the flame $2CO + O_2$, which burns at a pressure of 100 mm. and has a temperature somewhat exceeding 1000°K., show[1] that the concentration of excited molecules of CO_2 -- the carriers of the spectrum of the flame -- in this case exceed the equilibrium concentration by 10^{19} times. The chemical origin of the emission of rarefied flames of carbon monoxide is also an explanation for the fact that the yield of light in this case is practically completely independent of the temperature of the flame.[2] The possibility is not eliminated that the emission of the normal flame of CO ($p = 1$ atm., $T = 2000^\circ K.$) also represents to a significant degree chemiluminescence.

Exactly the same intensity of the bands of hydroxyl in the spectrum of the rarefied flame of hydrogen ($p = 10$ mm., $T = 1000^\circ$) proves to be a minimum of 10^{12} times greater than the intensity of equilibrium emission under the conditions of this flame.[3] Finally, measurements of the absolute intensity of the emission of rarefied flames of carbon disulfide give an intensity 10^{15} - 10^{16} times in excess of the intensity of the equilibrium emission.[4]

No less convincing a criterion permitting the elucidation of the nature of the emission of one flame or another is the distribution of intensity in its spectrum. Thus, for example, measurements of the relative intensities of the bands of hydroxyl 3064 ($0'' \, 0'$), 2875 ($1'' \, 2'$), and 2811 ($0'' \, 1'$) in the spectrum of the rarefied flame of hydrogen give the following figures: 1:0.105:0.09, while in the case of a purely thermal nature of the emission we should have had 1:0.00007:0.002 at $1000^\circ K.$ (the temperature of the flame) and 1:0.004:0.02 at $2000^\circ K.$[3] From a comparison of these numbers we see that the actual distribution of intensity has nothing in common with a distribution calculated according to Boltzmann.

In a number of cases the nonequilibrium character of the emission is also evident from the distribution of intensity among rotational lines of the bands, which leads to an effective "rotational temperature" which differs considerably from the temperature of the flame. This is true for the spectrum of hydroxyl in the case of rarefied flames of hydrogen[2] and acetylene,[5] as well as in the case of Bunsen and acetylene-air flames.[6] In the latter case, measurements of the distribution of intensity among the rotational lines of the OH band 3064 Å in the spectrum of the inner cone of the flame lead to a "rotational temperature" of 5000 - 6000°K., which exceeds the true temperature of the flame (2100°K. -- inner cone of the Bunsen flame and 2600°K. -- inner cone of the acetylene-air flame) by two to three times. The same "rotational temperature" of dicarbon, C_2, in the spectrum of the inner cone of the oxyacetylene flame, according to the measurements of Wolfhard,[6] proves to be equal to 5160°K., while the true temperature of the cone in the case of this flame comprises 3300°K. Let us add that the nonequilibrium character of the emission of C_2 is also indicated by the data of Johnson[7] pertaining to the Bunsen flame; to wit, Johnson found that the distribution of oscillatory energy in C_2 molecules deviates substantially from the Boltzmann distribution (the "oscillatory temperature" of C_2 measured by Johnson is equal to 5000°K.*).

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*We must observe that in contrast to the cases under consideration, the "rotational temperature" of hydroxyl in the oxyhydrogen[8] and oxyacetylene[6] flames proves to be close to the true temperature of the flame, from which it follows that there is an equilibrium character of the emission of hydroxyl in the case of these flames.

Another distinguishing characteristic of nonequilibrium emission is the presence of extinguishment, similar to the extinguishment of fluorescence. The extinguishment of chemiluminescence explains the characteristic drop in the yield of light with an increase in the pressure in the reaction zone, which is observed in many cases. Such a drop in the yield of light with an increase in the pressure of the oxygen can, in particular, be established from the data of Ouellet,[9] who studied the luminescence in the oxidation of phosphorus vapors. According to Ouellet, the constant of extinguishment of the carriers of the luminescence he observed is equal to $4 \cdot 10^{-3}$ mm.$^{-1}$, from which, on the assumption that the average lifetime of excited molecules is equal to 10^{-8} sec., a quite plausible quantity of the order of 0.1 is obtained for the probability of extinguishment (calculated on the basis of one collision).

The extinguishment of chemiluminescence was also detected by us in the case of the flame of carbon monoxide.[10] From our data the following values are obtained for the constant of extinguishment of excited molecules of CO_2 by various gases (for temperatures of about 1000°K.):

gas	CO_2 CO_2	O_2	N_2	H_2O*
constant of extinguishment in mm^{-1}	0.034	0.162	0.28	7.6

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*In work devoted to the study of the influence of moisture on the yield of light in the case of the flame of CO (Zh. Fiz. Khim.

(Journal of Physical Chemistry), **11**, 331, 1938), we interpreted the decrease in the yield of light with an increase in the moisture content of the mixture as an indication of a change in the chemical mechanism of the reaction. However, at this moment, as a result of newly performed experiments on the influence of moisture on the rate of combustion of CO, we are inclined to postulate an independence of the reaction mechanism on the moisture content, ascribing the influence of moisture on the yield of light to a simple extinguishment of chemiluminescence.

From these data it follows that the greatest extinguishing action is possessed by water. Assuming that the probability of extinguishment in this case is equal to 1, we find for the average lifetime of an excited molecule of CO_2 a quantity $\tau = 2\cdot10^{-6}$ sec. The unusually large value of this quantity is in complete agreement with the conclusion of Mulliken[11] that the transition to which the emission of CO_2 under consideration is related is a forbidden transition (apparently ${}^3\Pi \rightarrow {}^1\Sigma$).

Finally, we have also established the extinguishment of chemiluminescence in the case of the rarefied flames of hydrogen.[12] The drop in the yield of light with an increase in the pressure of the detonating mixture observed in this case is sufficiently well described by the well-known constant of extinguishment for hydroxyl (extinguishment by water vapors), equal to 10 mm.$^{-1}$.

Let us add that in the presence of mercury vapors in the zone of combustion of CO we observed a sensitization of chemiluminescence by mercury[13] (similar to the sensitization of fluorescence) — a phenomenon which is also characteristic of nonequilibrium emission.

Thus a large number of experimental facts give evidence that the emission of a number of flames — both rarefied, comparatively low-temperature flames and the normal flames — represent practically pure chemiluminescence.

In contrast to all the stable forms of luminescence, the mechanism of excitation of which can be considered essentially revealed, the mechanism of excitation of chemiluminescence, i.e. the mechanism of conversion of chemical energy freed as a result of various elementary processes to energy of electronic excitation of the corresponding molecules, still seems, to a considerable degree, to be an unresolved problem. Considering the processes of excitation of chemiluminescence as a rotation of processes lying at the basis of the mechanism of extinguishment of fluorescence (collisions of a second type), it is possible to postulate the following two basic mechanisms of excitation.

A number of considerations indicate that the extinguishment of fluorescence is often related to the dissociation of the extinguishing molecule. Such, in particular, is the mechanism of the extinguishment of fluorescence of mercury by hydrogen:

$$Hg'(^3P) + H_2 \longrightarrow Hg(^1S) + 2H.$$

The reverse of this process is the process:

$$2H + Hg \longrightarrow Hg' + H_2,$$

in which the chemical energy liberated as a result of recombination of H atoms is converted to energy of electronic excitation of the Hg atom. The mechanism of excitation of chemiluminescence, which is related to the recombination of various molecules, can be called the recombination mechanism. Here it is not essential that just the third partner of the collision be excited in the process of recombination. Indeed, considering the process of recombination as the reverse of the process of induced predissociation, for example, the process:

$$I_2' + M \longrightarrow 2I + M$$

(M is any particle), we should conclude that in the process of recombination, excitation of the newly formed molecule itself can also take place. The possibility is not eliminated that there is just such a mechanism of excitation of hydroxyl in the combustion zone, where the concentration of atoms of H and O is sufficiently great. There is no doubt that the recombination mechanism:

$$CO + O + M \rightarrow CO_2' + M \quad \text{or} \quad CO + O \rightarrow CO_2'$$

lies at the basis of the excitation of luminescence of the flame of CO. A weighty argument in favor of this mechanism is the fact that under the conditions of the combustion of CO the process $CO + O = CO_2$ is the elementary process whose thermal effect is closest to the energy of excitation of the CO_2 molecule. The correctness of this mechanism is also confirmed by investigations of the emission which accompanies the low-temperature oxidation of CO by ozonized oxygen (see below).

A second mechanism of the excitation of chemiluminescence is obtained as the reverse of the process of extinguishment in which the excited molecule enters into an exchange reaction with the extinguishing molecule. Such, for example, is the process:

$$Hg' + H_2 \rightarrow HgH + H$$

This mechanism of excitation can be called the exchange mechanism.

The exchange mechanism lies at the basis of the excitation of luminescence of a large number of flames. Thus, according to Polanyi and Schay,[14] the excitation of the spectrum of an alkali metal (Me) in the zone of highly rarefied alkali halide flames is related to the processes:

$$X + Me_2 \rightarrow MeX^* + Me$$

$$\text{and} \quad MeX^* + Me \rightarrow MeX + Me'$$

(X is a halogen atom). Here as a result of an exchange reaction of an atom X with a molecule Me_2, energy-rich (excited) molecules MeX appear; they transfer their energy to an atom of Me by means of a collision of the second type. Analogous to this is the mechanism of the excitation of chemiluminescence in the reaction of halide salts of mercury with alkali metals, where we have the following combination of processes:

$$HgX + Me \rightarrow MeX^* + Hg$$

$$MeX^* + Me \rightarrow MeX + Me'.$$

One of the essential conditions determining the possibility of the exchange mechanism of excitation of chemiluminescence is the sufficiency of the thermal effect of the reaction for the excitation of the corresponding spectrum. In the preceding examples this condition is fulfilled thanks to the comparatively low stability (lability) of the molecules Me_2, HgX, and HO_2.

In the flames of hydrocarbons we must assume, on the basis of spectroscopic data, the presence to a sufficient degree of the labile radical HCO; the excitation of hydroxyl can also be related to the exchange reaction of this radical with atomic oxygen:

$$HCO + O \rightarrow CO + OH'.$$

We might have been able to attempt to explain a number of other cases of excitation of chemiluminescence (for example, the appearance of the spectra of the radicals CH and C_2, which are normal for the flames of hydrocarbons) with the aid of exchange reactions of analogous labile intermediate substances; however, our information both on the substances of this type themselves and on those elementary processes in which they participate is still insufficient by far for the construction of any well-grounded mechanism of the excitation of chemiluminescence in every concrete case.

Together with direct excitation of the carriers of the spectrum of chemiluminescence immediately in the process of the elementary chemical reaction itself, secondary excitation of these carriers should also be considered probable. We have already had examples of this type of secondary excitation in the case of highly rarefied flames, where the energy-rich molecules of MeX* which appear as a result of the primary exothermic process do not themselves appear to be carriers of the spectrum of chemiluminescence. The carriers of the spectrum (excited atoms of Me) here appear only as a result of a secondary process ($MeX^* + Me \rightarrow MeX^* + Me'$). The case mentioned above of the sensitization of chemiluminescence by mercury can also be considered as an example of secondary excitation of chemiluminescence. The corresponding secondary process in this case is obviously connected with a collision of the second type, the participants of which are an excited molecule of CO_2 and an atom of mercury:

$$CO_2' + Hg \rightarrow CO_2 + Hg'.$$

However, cases of secondary excitation of chemiluminescence apparently rare enough. We arrive at this conclusion on the basis of the following considerations. The carriers of the spectrum of chemiluminescence in the oxidation of sulfur and the sulfur-containing compounds CS_2, H_2S, and COS are the radicals S_2, OH, CS, and SO, whose energy of excitation comprises, respectively, 90.0, 92.1, 110.0, and 111.0 Cal. If a secondary excitation took place in the reaction zone, then together with the spectra of these radicals we should also have expected the appearance of intense spectra of the SO_2 molecules, which are present in the reaction zone in immeasurably large concentrations and possess an energy of excitation close to that cited above (90.5 Cal.). Meanwhile the bands of SO_2 are completely absent in the spectra of the flames specified. Secondary excitation of chemiluminescence seems improbable to us for the additional reason that a strong dispersion of the energy of the energy-rich molecules which appear first must be assumed in the combustion zone as a result of their collisions with the surrounding molecules. This dispersion is considerably worse under the conditions of highly rarefied flames, in the case of which, for example, an insignificant admixture of nitrogen (in a quantity of several tenths of a millimeter) leads to a sharp decrease in the yield of light.[14]

In a number of cases <u>continuous</u> spectra of chemiluminescence are observed. Of course, some of them prove upon more thorough investigation to have a discrete line-band structure. Such, in particular, is the "continuous" spectrum of the flame of CO, which proved, upon the use of a spectral apparatus of sufficiently high resolving power, to consist in fact of a large number of closely situated bands.[15] The visible spectrum of the hydrogen flame also exhibits the same quasi-continuous appearance. According to the research of Pavlov,[16] this spectrum should with a high probability be ascribed to hydroxyl. However, cases of chemiluminescence are known where the continuous character of the spectrum is not open to doubt. Such, for example, is the spectrum of chemiluminescence observed by Polanyi and Schay[17] in the reaction of the alkali metals with SnX_4. According to these authors, the continuous spectrum here is related to the process:

$$2SnX_3 \longrightarrow SnX_2 + SnX_4 + h\nu.$$

According to the calculations of Polanyi and Schay, the thermal effect of this reaction comprises approximately 70 Cal., which is in close agreement with the energies corresponding to the short-wave limit of the continuous spectrum under consideration.

A continuous spectrum (together with the discrete spectra) is also observed in the emission of the flames of sulfur and sulfur-containing compounds. The short-wave limit of this spectrum lies at about 3000 Å (95 Cal.). As in the case of the majority of continuous spectra, here also the act of emission evidently coincides with an act of chemical conversion, a fact which is confirmed by the independence of the yield of light on the pressure which we have established.[4] However, as regards the concrete chemical mechanism of the process to which the emission of the continuous spectrum is related, in this case we can as yet construct only more or less probable hypotheses.

Let us indicate also that cases of emission of continuous spectra upon direct recombination of atoms or radicals are theoretically possible. Such processes can be considered as the reverse of photochemical dissociation. We should state, however, that the probability of recombination accompanied by emission is very small,[18] a fact to which the comparatively small extent of the continuous spectra of chemiluminescence should apparently be ascribed. As an example of a continuous spectrum related to the recombination of atoms, we can indicate the spectra observed in flames containing the halogens.[19] These spectra are due to the process:

$$X + X' \longrightarrow X_2 + h\nu$$

(X' is a metastable halogen atom).

Thanks to the low probability of direct recombination of atoms and radicals, the yield of light in the region of the continuous spectrum of emission should be low in comparison with the yields of light in the region of the discrete spectra. It is possible that the fact that the continuous spectra of flames usually represent only a comparatively weak background on which considerably more intense bands (or lines) of the discrete spectrum emerge should be ascribed to this circumstance.

As for the absolute yields of light in general in the case of chemiluminescence, here we can cite the following figures, which are the result of the measurements performed by us on various flames. In our experiments the number of quanta emitted, related to the number of reacted molecules, was taken as the measure of the yield of light (i). The yield of light in the case of the rarefied flames of hydrogen is comparatively small.[3] Here one quantum is emitted for approximately every 10^6 reacted molecules of H_2. Taking into consideration the extinguishment of chemiluminescence, we obtain in this case one excited molecule of OH for every 10,000 reacting molecules of H_2. The yield of light in the case of CO flames, which, as is well known, are among the most actinic flames, is considerably higher. Here the quantity i comprises about 10^{-3}, i.e., one quantum of light is emitted for approximately every 1000 reacted molecules of CO. There is an even higher yield of light in the case of the flame of carbon disulfide:[4] the maximum yield of light measured by us comprises here 1/40, i.e., one quantum for 40 reacted molecules of CS_2.

In contrast to the cases considered, where the yield of light either practically does not depend at all on the temperature or depends very weakly on it ($CS_2 + O_2$), in the case of the reaction of CO with ozonized oxygen we have a sharp exponential increase in the value of i with the temperature of the flame;[20] here at 150°C. we have $i = 10^{-5}$ and at 250°C. $i \cong \frac{1}{2} \cdot 10^{-3}$, which gives one excited molecule of CO_2 for every 1000 reacting molecules of CO at 150°C. amd one excited molecule for 20 reacting molecules at 250°C.

The carriers of the spectra of chemiluminescence appear in the reaction zone as a result of various elementary chemical processes which enter into the complex mechanism of the reaction. Hence there should be a definite, well-defined connection between the concentration of the carriers and the rate of the reaction. The presence of such a connection is indicated, in particular, by the measurements of the distribution of the intensity of OH emission and of the distribution of the reaction product H_2O along the zone of the stationary rarefied flame of hydrogen, performed by Slakov.[21] From the data of Slakov it follows that the maximum of the concentration of excited hydroxyl (obtained while taking into consideration the extinguishment of chemiluminescence) coincides with the maximum of the reaction rate. This agreement of the maxima of the OH concentration and the reaction rate takes place in the case of mixtures of various concentrations ($2H_2 + O_2$, $H_2 + O_2$, and $H_2 + 2O_2$).

From the data cited it follows that a simple relationship should exist between the concentrations of the carriers of the spectrum of chemiluminescence and the rate of the reaction. It is most natural to assume that there is a direct proportionality between the concentrations of the carriers and the reaction rate, an assumption which in fact does find direct experimental confirmation. To wit, by measuring the relative intensities of the band of hydroxyl 3064 Å in the spectrum of the rarefied flame of acetylene at various pressures and compositions of the combustible mixture, Avramenko[5] found that for every composition of the mixture there is a linear dependence of the concentration of the excited hydroxyl molecules (calculated from the measured intensities of the emission by means of a consideration of the extinguishment of chemiluminescence) on the pressure in the reaction zone. On the other hand, Avramenko showed that the reaction rate (measured according to the amount of water formed after a definite interval of time) also varies with the pressure of the mixture according to a linear law. From this it follows that the concentration of excited hydroxyl in the zone of combustion of acetylene is proportional to the reaction rate.

It is interesting to indicate that according to the measurements of Avramenko the concentration of unexcited hydroxyl in the acetylene flame (measured according to the absorption spectrum of hydroxyl) also proves to be proportional to the reaction rate. Introducing a purely formal factor of excitation of hydroxyl F, the concentrations of excited and unexcited hydroxyl can be related by the following ratio:

$$(OH') = F \cdot (OH).$$

According to the data of Avramenko, the quantity F remains approximately constant in all regions of steady combustion of acetylene and depends neither on the pressure nor on the composition of the combustible mixture. This experimental fact is of extremely vital significance. First of all, it gives evidence of the constancy of the chemical mechanism of the reaction in the whole region of steady combustion of C_2H_2. Furthermore, it permits the substitution of considerably simpler measurements of intensities in the emission spectrum for the complex and often impossible (in the case of low concentrations of OH) measurements of relative concentrations of hydroxyl. In particular, the constancy of the quantity F permits the study of the distribution of hydroxyl in the reaction zone (according to the intensity of the emission), i.e., the resolution of a problem which is extremely important for chemical kinetics and which, at least in the case of rarefied flames, is insoluble by other methods. Finally, as a result of the experiments of Avramenko we have a good basis for making definite conclusions on the concentration of the various intermediate substances on the basis of the intensities of the spectra of chemiluminescence, which has constantly been done without any such grounds.

As for the absolute magnitude of the factor of excitation of hydroxyl, we can evaluate it on the basis of the following data pertaining to the rarefied flame of hydrogen, assuming that here also there is a proportionality between the concentration of the excited hydroxyl and the rate of the reaction (the proportionality of the concentration of the excited hydroxyl and the reaction rate in this case was also experimentally demonstrated by Avramenko). According to the measurements of Ziskin and Kondrat'yev,[3] the concentration of excited hydroxyl in the zone of the rarefied flame of hydrogen, which burns at a pressure of about 10 mm., corresponds to a partial pressure of the order of $5\cdot10^{-8}$ mm. According to the same authors, the concentration of unexcited hydroxyl in this flame corresponds to a pressure of the order of 0.1 mm. From this we obtain for the factor F, $5\cdot10^{-7}$ — a quantity 10^{14} times larger than the Boltzmann function $e^{-\frac{92,100}{RT}}$ (cf. above).

The proportionality of the concentration of the carriers of the spectrum of chemiluminescence to the reaction rate also exists in the case of the CO flame. This proportionality is manifested in the constancy of the "maximum" yield of light i_o (i.e., the yield of light which should have existed in the absence of extinguishment of chemiluminescence), related to the measured yield of light i by the relationship:

$$i = \frac{i_o}{1 + kp},$$

where k is the constant of extinguishment. Our investigations of the CO flame[22] show that the quantity i_o remains constant in the rather broad interval of pressure, temperature, composition of the mixture, and degree of its humidity which we studied (see note to p. 5). In our opinion, this constancy of the quantity i_o indicates that the chemical mechanism of the reaction is unchanged in the region of combustion studied.

A list of luminescent reactions, even if limited only to gas reactions, would be extremely diverse. The majority of the cases are luminescences of flames. However, luminescence is frequently observed in the case of the so-called slow reactions. Thus, the weak luminescence which accompanies the slow oxidation of carbon monoxide outside the region of combustion is well known. We also had an opportunity to observe an analogous luminescence in the reaction of conversion of water gas (moist carbon monoxide, p=1atm., t°=700°C.). Furthermore, a weak luminescence accompanies the slow reaction of oxidation of sulfur monoxide.[23] The slowness of this reaction may be judged by the long duration of the luminescence. Thus, at 50°C. the duration of the luminescence reaches 30 sec. Manometric investigations indicate that the reaction of oxidation of sulfur monoxide does not cease with the disappearance of visible luminescence. This compels us to assume that the excitation processes also take place after the disappearance of luminescence; however, the concentration of excited particles in this case is lower than the minimum observable concentration. Evidently we also have an analogous situation in the transition from the cold flame of hydrocarbons to the reaction of slow oxidation, which is not accompanied by noticeable luminescence. The following fact, in particular, speaks in favor of the hypothesis expressed above. Using a biological method developed by Prof. A. G. Gurvich for the recording of emission, Ziskin and Tverskiy (unpublished work) succeeded in detecting hydroxyl emission in the reaction of slow oxidation of hydrogen ($p=1$ atm., $t^\circ \cong 500^\circ$C.). The intensity of the emission in this case lies at the threshold of the sensitivity of the usual protographic method. The observed hydroxyl emission in the slow oxidation of hydrogen is a direct indication of the presence of processes of excitation under the conditions of a slow reaction as well.

Investigations of chemiluminescence do not have independent value. The basic task of these investigations consists of revealing the intermediate substances and the individual elementary processes, i.e., in the end result — the establishment of the chemical mechanism of the reactions. Very little has as yet been done in this direction; however, in a number of cases investigations of chemiluminescence have played a definite positive role. Here we should indicate first of all highly rarefied flames, for the establishment of the mechanism of which investigations of chemiluminescence have been of decisive significance. Furthermore, these investigations have led to the discovery of a great number of labile intermediate substances, without a knowledge of which the construction of a chemical mechanism of the reaction would be inconceivable. Let us indicate, for example, hydroxyl and atomic oxygen, whose presence in the zone of combustion of CO and definite role in the mechanism of the reaction follow directly from the spectra of chemiluminescence of the CO flame. Investigations of the luminescence of the flames of CO and H_2 have also permitted the establishment of the predominat- role of the surface reaction close to the lower limit of ignition of these gases, which indicates that the generation of the reaction takes place on the surface of the reaction vessel. Let us indicate also that investigations of chemiluminescence in the case of the oxidation of CO by ozonized oxygen have permitted the formulation of the chemical mechanism of this reaction. We hope that further, particularly quantitative, investigations of chemiluminescence will play a large role in the resolution of the basic problem of chemical kinetics — the problem of constructing a chemical mechanism for the most important gas reactions.

Summary

Characteristic of chemiluminescence as nonequilibrium emission are a number of indications, according to which the chemical origin of the emission can be established in each individual case. The basic physical criteria of luminescence are the following: an excess of absolute intensity of emission over intense thermal emission, a non-Boltzmann distribution of the intensity in the spectrum of luminescence, and the presence of extinguishment of luminescence. The study of rarefied, comparatively low-temperature flames practically without exception, as well as of a number of normal flames, is based on these criteria of chemiluminescence.

The mechanism of the excitation of chemiluminescence, i.e., the mechanism of the conversion of chemical energy into energy of electronic excitation of the carriers of the spectra of chemiluminescence, can be obtained as the reverse of processes of extinguishment of fluorescence. Two basic concepts of the mechanism of excitation of chemiluminescence are: the recombination mechanism, consisting of the excitation of the carrier as a result of the recombination of free atoms or radicals, and the exchange mechanism, related to the exchange chemical reaction. In various luminescent reactions one mechanism or the other is realized. In most cases primary excitation of luminescence, i.e., excitation directly in

the process of the elementary reaction itself, predominates. Processes of excitation take place both in the case of rapid (flames) and in slow reactions. The fact that luminescence in the case of certain slow reactions is not observed is due to the low concentration of the carriers.

The chemical origin of chemiluminescence is manifested in the presence of a direct relationship of the concentration of the carriers of the spectrum of chemiluminescence and the rate of the reaction. In individual cases the concentration of the carriers proves to be proportional to the reaction rate. The independence of the proportionality factor on various other factors (pressure, temperature, composition of the mixture, impurities) appears to be a criterion for the invariability of the reaction mechanism.

Investigations of chemiluminescence are essential for the construction of the chemical mechanism of the reaction.

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