It is the purpose of this note to present an evaluation of the experimental evidence for and against "anomalous" temperatures of OH in flames. Experimental studies have been carried out on low pressure flames and on flames burning at atmospheric pressure. The results have usually been interpreted by using relations which are applicable only to isothermal systems. Attempts to correct for self-absorption have been made by using isointensity methods. For spectral lines with Doppler contour it has been demonstrated by quantitative calculations that the isointensity methods do not correct for self-absorption unless self-absorption is weak. In particular, Shuler's method, without allowance for the effect of frequency on intensity, has been shown to yield nonlinear plots for strong self-absorption and to be inferior to conventional procedures in the absence of self-absorption. Extensive studies on the effect of self-absorption in falsifying experimental data have been carried out by Cowan and Dieke.

We have recently attempted to estimate absolute emission intensities for OH in low pressure flames by using data obtained by Oldenberg and Rieke.

During the course of this work we have realized that the use of the customary isothermal relations may yield plots which are either nonlinear or, if linear, may yield meaningless results. Unfortunately, the matter has been allowed to rest at this point. Thus, it is not uncommon to use relations applicable to isothermal systems with negligible or small self-absorption and to base conclusions on what could be spurious effects. One might, therefore, start further discussion by noting that claims for the validity of anomalous flame temperatures are based on experimental evidence which is practically uninterpretable in a quantitative and convincing manner. This last statement is especially true for observations made at atmospheric pressure of the "inner cone" of flames, i.e., of the region in which strong temperature gradients exist. At atmospheric pressure the thickness of the flame front may be no larger than the slit-width of the spectrophotograph. A significant improvement over this type of investigation has been registered by the low pressure flames of Gaydon and Wolfhard since, at low pressures, temperature gradients normal to the direction of observation can be minimized.

If we neglect, for the time being, the unhappy circumstance that we always observe regions of active combustion through cooler gas layers, there are, to begin with, discrepancies between the conclusions reached by different investigators. For example, Shuler quotes Duleck and Crosswhite as having shown that the "anomalous" intensity distributions of OH observed in some atmospheric pressure flames are principally the result of self-absorption. On the other hand, Gaydon, in summarizing the available information on OH, speaks of effective rotational temperatures for OH around 5700°K at atmospheric pressure and still higher temperatures at very low pressures. The important pioneering work of Gaydon and Wolfhard on low pressure flames has been checked recently; however, the experimental conditions were such that the observed "anomalies" could be explained readily on the basis of self-absorption.

Shuler, in quoting Broida's anomalous rotational temperatures in flames burning at atmospheric pressure, expresses the opinion that "corrections" for self-absorption can be made simply by measuring the intensity of absorption by the flame for continuous radiation. This argument is very weak, however, since absorption measurements for continuous radiation bear a close relation to self-absorption only if the experimental slit-width is small compared to the width of the spectral lines under study. This condition is probably not satisfied in Broida's work in spite of Broida's excellent spectrographic techniques.

The preceding discussion emphasizes the fact that there is at present no direct and unequivocal evidence for the existence of "anomalous" rotational or vibrational temperatures of OH in flames. On the other hand, indirect support for the existence of "anomalies" has been obtained, particularly by Gaydon and Wolfhard. Nevertheless, in view of the ever-present problems arising from the existence of temperature gradients in the field of view and the equally unavoidable possibility for falsification of data as the result of self-absorption, the indirect and inferential evidence is never quite satisfying. Furthermore, even in the absence of analytical treatments on the combined effects of self-absorption and temperature gradients in producing distortions, it is frequently possible to offer plausible explanations for observed data without the invention of "anomalous" rotational temperatures for OH. For example, a decrease in apparent population temperature from the base to the top of a flame may indicate either higher temperatures of OH or else higher concentrations of OH at the base of the flame. Similarly, "normal" temperatures for OH in H2-O2 flames but 'abnormal' temperatures in the OH flames containing a trace of acetylene may indicate either chemiluminescence or else the initial production of large quantities of OH as the result of introduction of the acetylene. The calculations on the effect of self-absorption in conventional plots used for the determination of population temperatures in flames, have shown clearly that the apparent rotational temperatures are a very sensitive function of the absolute concentration of OH. Hence, even a relatively small excess of OH at the base of a flame could be responsible for a relatively high value of the population temperature. Perhaps the strongest case for the reality of the "anomalies" can be made on the basis of the increase in rotational temperature with a decrease of pressure. But even this result is not unambiguous without a careful quantitative study of the optical system, of changes in the field of view and of temperature gradients with pressure, etc. Although we have no objections, in principle, against "anomalous" temperatures and no prejudice other than that we believe that "anomalies" should be established beyond any reasonable doubt, it is our considered opinion that the available experimental evidence in support of abnormal rotation or vibration of OH in the \( \text{O}_2 \) state in flames is not overwhelming.

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