SUMMARY.

The work presented in this thesis comprises of the spectroscopic study of methyl alcohol-air flames. Observations have been made of intensities of various spectral radicals present in the flames and on temperatures as the air content of the burning mixture is varied in known proportions with a view to follow the processes of combustion taking place in the flames (Chapter I).

A brief and critical survey of various methods used in the spectroscopic study of flames and the results obtained therefrom, have been presented with emphasis on the limitations, approximations and the gaps in these studies (Chapter II).

The need for the study of methyl alcohol air flame arises on account of the facts (i) that this flame is the only normal flame emitting HCHO bands which are characteristic of cool flames and (ii) that no systematic study of variation of intensity of spectral emissions and of temperatures in these flames is available. The data obtained to attain this objective may give a coherent picture of the combustion phenomena in these flames in conjunction with the available, mostly scattered information (Chapter III).
Experimental set-up.

An assembly was developed based on earlier work in this laboratory to obtain flames of graded air/fuel ratio. With proper metering of alcohol and air, the air/fuel ratios could be determined with reasonable accuracy. The metered alcohol was vaporized and the vapour mixed thoroughly with air and then fed to the Bocker burner, whose usual air inlet control was closed to allow feeding of known mixtures to it. The heating of alcohol vaporizing and mixing chambers was done electrically through an electronic temperature control device. With this arrangement and devices the flames obtained were found steady over a long stretch of period (Chapter IV).

Intensity Measurements

The spectrum of the inner cone was found to contain $C_2$(Swan) (in traces) CH (4315 A° and 3900 A°), CH (3064 A°), cool flame and CO-flame bands, OH being the strongest feature of the spectrum. The intensities of $C_2$ CH and OH were measured photographically and also photo-electrically with a view to assess the facility and accuracy of these methods. The CO-flame bands and cool-flame
bands are weak, diffuse and are covered by continuum and hence they could not be subjected to quantitative study. However, intensity at $4110 \text{ A}^0$ has been measured and is taken to represent intensity of the continuum. The intensities of the above mentioned bands vary with air/fuel ratio, attaining their maximum value on the fuel-rich side of stoichiometric mixture.

$\text{C}_2$ intensity is the first to disappear as the air content of the flame is increased and is the first also to attain its maximum value. CH and CH respectively attain their maxima as the air content is increased.

Peak and integrated intensities of OH have also been measured with a view to examine the effect of rotational temperature on intensity measurements (Chapter V).

**Line reversal temperatures.**

Sodium has been introduced into the flame by the sparking method which is found to be convenient and satisfactory. Sodium line reversal temperatures have been measured using a calibrated strip filament lamp as the background source, in conjunction with traditional optical system and Hilger constant deviation spectrograph. Sodium reversal temperatures so obtained were duly corrected for colour and absorption. The corrected values of tempera-
tures were observed to vary with air/fuel ratio from 1800°K to 1900°K for inner cones and 2000°K to 2140°K for outer cone. The maxima were found on the rich side of stoichiometric mixture (Chapter VI).

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**OH Temperatures.**

Rotational temperature of OH was determined by measuring the intensity of four lines from the \( R_1 \) branch. A case has been made out for adoption of this procedure. The values so obtained are, in general, high (~2800°K) and are found to vary with air/fuel ratio in the range 2730°K to 2990°K. The maximum temperature occurs on the rich side of stoichiometric ratio.

Estimate of the vibrational temperature has been made by comparing the intensities of the heads of (2,1) and (1,0) bands. This comes out in the order 3180°K and shows no appreciable variation with air/fuel ratio.

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**Conclusions.**

Results on reversal temperature are found to be of the order of known adiabatic flame temperatures which may be taken to mean that sodium reversal method yields normal values of temperature. The location of temperature
maximum on the fuel-rich side of the stoichiometric mixture is ascribed to dissociation losses, diffusion by atmospheric oxygen and the increasing dilution by nitrogen with increasing air content.

The comparatively high values of vibrational and rotational temperatures and almost negligible variation of the former with air/fuel ratio indicates OH emission as chemiluminiscent. On the other hand the variation of rotational temperature with air/fuel ratio suggests thermal excitation of OH. The latter conclusion is further supported by the coincidence of reversal temperature maximum with rotational temperature maximum. Thus OH may be considered to be formed in the excited state directly through chemical reaction, or it may be formed in the ground state and then excited through collision with other high energy species in the flame.

The critical assessment of the various methods of measuring intensities has been done to justify the convenience and accuracy of photoelectric method. Using this method it is shown from the results that the relation between peak and integrated intensities is affected by the rotational temperature. For that reason, it is imperative to take into account the effect of rotational
temperature on the band head, if the peak intensities are to represent the true band intensities.

The behaviour found for intensity variation of various radicals with air/fuel ratio has supported the following reactions:

\[
\begin{align*}
G_2 + OH & \rightarrow CH^* + CO \\
CH + O_2 & \rightarrow OH^* + CO \\
\text{and} \quad CO + O + M & \rightarrow CO_2^* + M
\end{align*}
\]

Further the critical analysis of the present study and similar studies by other workers point to the possibility of the following mechanisms for formation and excitation of various radicals in these flames in addition to above reactions.

(i) \( CO + NO \rightarrow CO_2 + OH \)

\( \text{OH} \rightarrow OH^* \) (through a suitable collision)

(ii) \( CH_3OH + O_2 \rightarrow CH_3OO + OH \) for the formation \( CH_3OO + M \rightarrow HCHO + OH + M \) of HCHO

(iii) \( C_2 \) formed possibly through endothermic reactions.