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THE THEORETICAL FLAME TEMPERATURES OF SOME PROPANE/AIR AND ETHYLENE/AIR MIXTURES ENRICHED WITH OXYGEN

by

K. N. Palmer

SUMMARY

Calculated values of the flame temperatures of some propane and ethylene flames are given, together with an outline of the method of calculation. The temperatures of flames enriched with oxygen are appreciably greater than those for mixtures of fuel with air only.

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Fire Research Station,
Boreham Wood,
Herts.

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INTRODUCTION

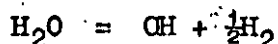
In theoretical considerations of the quenching of gas and vapour explosions by means of flame arresters it is of importance to know the temperature of the flame. Clearly, if the quenching action is due to the cooling of the flame by the surface of the arrester, then the difference in temperature between the flame and the arrester will govern the rate of flow of heat. The theoretical flame temperatures may be calculated from values of the heat liberated during the combustion and values of the chemical thermodynamic properties of the flame gases, assuming no heat losses. As the thermodynamic properties are usually derived for constant pressure conditions it is usual to evaluate flame temperatures on a constant pressure basis; this procedure has been followed in the present note.

The flame temperatures of various propane/air mixtures have been listed by Smith, Edwards, and Brinkley⁽¹⁾, and corresponding values for ethylene/air mixtures were published by Simon and Wong⁽²⁾. Values were however not available for various mixtures of propane, or ethylene, with air enriched with oxygen as had been used in experiments with gauze flame arresters⁽³⁾, and calculations of these temperatures are the subject of this note. As the flame temperatures of these mixtures are considerably higher than the temperatures obtained with most propane or ethylene mixtures with air, the dissociation of polyatomic molecules of flame gases into smaller molecules and radicals (e.g. CO, OH, H) becomes appreciable. Energy is required to produce these dissociations and so less remains available as thermal energy in the flame gases. The flame temperature is therefore less than it would be if no dissociation occurred. In the calculations given below, allowance has been made for dissociation of the flame gases.

METHOD OF CALCULATION

The procedure followed was that given by Gaydon and Wolfhard⁽⁴⁾. In this method a temperature believed to be near the value sought is assumed and the composition of the flame gases is calculated; the heat content of these gases is then obtained and compared with the total amount of heat liberated in the combustion. If these two quantities are not equal it can be seen whether the original temperature taken is above or below the true temperature. A second temperature is then assumed, the calculation repeated, and the true flame temperature obtained by interpolation.

In the calculation of the composition of the flame gases the equilibrium constants tabulated by Gaydon and Wolfhard⁽⁴⁾ were usually taken; an exception was the constant for the equilibrium



since better values could be derived from a later determination of the dissociation energy of the OH radical⁽⁵⁾. The improved values of the equilibrium constant are given in Appendix 1, together with an outline of the method of derivation.

Values of the chemical thermodynamic properties were taken from tables published by the U.S. National Bureau of Standards⁽⁶⁾.

FLAME TEMPERATURES

As previous workers may have used different methods of calculation of the flame temperatures of fuel/air mixtures, calculations were made by the present method for one fuel/air mixture of each fuel in order to compare the values obtained with those of the previous workers. The flame temperatures of propane/air mixtures, calculated by Smith, Edwards, and Brinkley⁽¹⁾, are given in Fig. 1 which also includes a value for a 4 per cent propane/air mixture calculated by the present method. The results of Simon and Wong⁽²⁾ for ethylene/air mixtures are plotted in Fig. 2, and this includes a value for a 6.5 per cent ethylene/air flame calculated by the present method. In both instances the temperatures calculated by the present method are within 10°K of the earlier values, and hence it has been assumed that the results of the various methods of calculation are strictly comparable.

Flame temperatures were then calculated for the following stoichiometric propane mixtures:

Propane 1 part by volume, oxygen 5 parts, nitrogen 15.1 parts.
" 1 " " " , " 5 " , " 7.6 "

and the values are shown in Fig. 3, where the flame temperature is plotted against the amount of nitrogen present. Flame temperatures are also shown in Fig. 3 for the following stoichiometric ethylene mixtures:

Ethylene 1 part by volume, oxygen 3 parts, nitrogen 7.5 parts.
" 1 " " " , " 3 " , " 4.7 "

The values given should be accurate to within $\pm 20^\circ\text{K}$.

CONCLUSION

The flame temperatures of some propane/air and ethylene/air flames have been calculated and good agreement was obtained with previous published values. Calculation was also made of the flame temperatures of propane/air and ethylene/air mixtures enriched with oxygen. With these mixtures the dissociation of the molecules in the flame gases became important.

ACKNOWLEDGEMENT

Miss J. S. Hall and Miss S. E. Townshend assisted in the calculations.

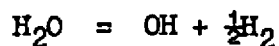
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2. SIMON, D. M., WONG, E. L. Flame velocities over a wide composition range for pentane-air, ethylene-air, and propyne-air flames. N.A.C.A. Research Memo E51 H09; Oct. 1951.
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APPENDIX 1

Values of the equilibrium constant (k) for the reaction



Temperature °K	k
2000	7.21×10^{-4}
2100	1.54×10^{-3}
2200	3.08×10^{-3}
2300	5.77×10^{-3}
2400	1.03×10^{-2}
2500	1.76×10^{-2}
2750	5.62×10^{-2}
3000	1.48×10^{-1}

These values were calculated from published information⁽⁶⁾ on the ratios $\frac{F_T^\circ - H^\circ}{T}$ for the reactant and products of the reaction at various temperatures, where F = free energy, H = heat content, T = temperature, first subscript (T or zero) indicates temperature, second subscript (r or p) indicates reactant or product, and superscript zero indicates the standard state.

Then let

$$\frac{F_{T,p}^\circ - H_{O,p}^\circ}{T} = \frac{F_{T,r}^\circ - H_{O,r}^\circ}{T} = b.$$

$$\text{i.e. } (F_{T,p}^\circ - F_{T,r}^\circ) = b T + (H_{O,p}^\circ - H_{O,r}^\circ)$$

Now $(F_{T,p}^\circ - F_{T,r}^\circ) = \Delta F_T^\circ =$ change in free energy in reaction at temperature T°K and $(H_{O,p}^\circ - H_{O,r}^\circ) = \Delta H_0^\circ =$ change in heat content in reaction at temperature 0°K

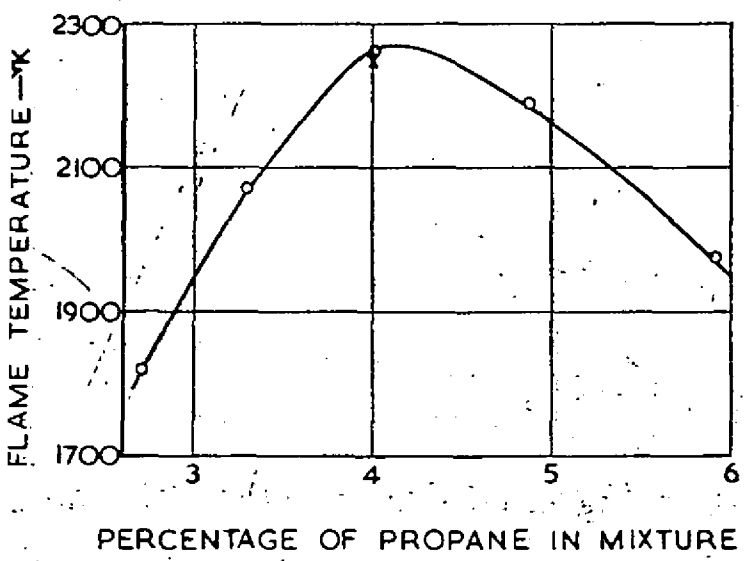
$$\Delta F_T^\circ = b T + \Delta H_0^\circ$$

$$\text{But } \Delta F_T^\circ = -R T \log_e k$$

So k may be calculated from

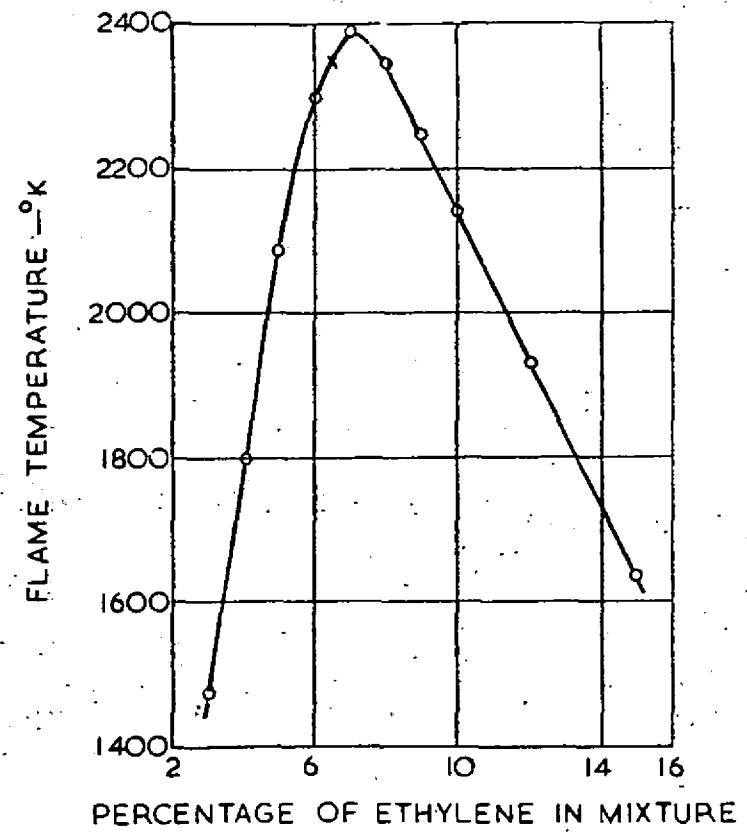
$$-R T \log_e k = b T + \Delta H_0^\circ \text{ using the published values }^{(6)}$$

of ΔH_0° .



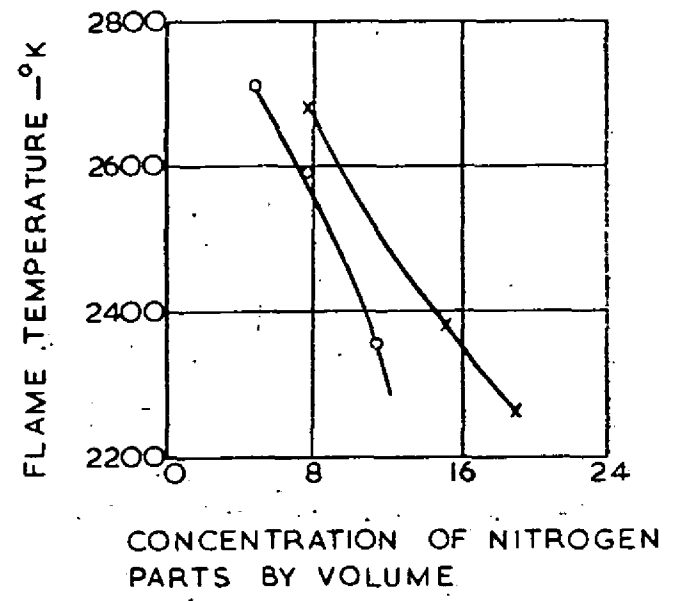
o Values taken from reference 1
 x Value calculated
 Unburnt gas at 25 °C

FIG.1. FLAME TEMPERATURES OF PROPANE/AIR MIXTURES



o Values taken from reference 2
 x Value calculated

FIG.2. FLAME TEMPERATURES OF ETHYLENE/AIR MIXTURES



o Ethylene: oxygen:: 1: 3 by volume
 x Propane: oxygen:: 1: 5 by volume

FIG.3. FLAME TEMPERATURES OF FUEL- OXYGEN - NITROGEN MIXTURES