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The Mechanism of Flame Propagation

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Recently Tanford and Pease have shown that in a number of carbon monoxide flames the burning velocity increases as the calculated equilibrium concentration of hydrogen atoms in the flame front increases. They point out that this would be so if the propagation of the flame were dependent on the diffusion of hydrogen atoms ahead of the flame. It is shown in the present paper that, by combining calculated ignition and flame temperatures, the variation in burning velocity with composition can also be accounted for on an essentially thermal theory of flame propagation.

IN a recent paper Tanford and Pease¹ have calculated the equilibrium concentrations of hydrogen atoms, hydroxyl, radicals and oxygen atoms in carbon monoxide flames to which have been added nitrogen, water, and hydrogen. Using burning velocities measured by Jahn² they show that the burning velocity increases regularly, on the whole, with the hydrogen atom concentration (see Fig. 1, reference 1). This most interesting and striking result is consistent with the view that the flame is carried from one layer to the next by the diffusion of the light and fast-moving hydrogen atoms ahead of the flame, for the flame will be expected to move more quickly the higher the equilibrium concentration of hydrogen atoms in the flame front. They have followed up this idea in two subsequent papers.^{3,4} In the first of these³ Tanford states that "this correlation is not readily explained by theories of burning velocity based on heat conduction."

The object of this communication is to show that the variation in burning velocity observed by Jahn is quite consistent with an essentially thermal conception of flame propagation.

The three main features of Jahn's results are that the burning velocity increases (a) when the percentage of carbon monoxide is increased, the

TABLE I. Flame temperatures, T_f ; ignition temperatures, T_i ; and burning velocities, V_b , for carbon monoxide-oxygen flames. The burning velocities are given in cm/sec.

Percentage composition			T_f	T_s^a						V_b Jahn
CO	O ₂	N ₂		A	B	C	D	E	F	
35**	8.5	56.5	1730	947	1212	968	1247	984	1273	25.5
261**	44.1	29.4	2320	1100	1475	1057	1398	1028	1347	29.5
40*	12.6	47.4	2320	1003	1304	1002	1303	1001	1302	30
40**	12.6	47.4	2320	955	1224	973	1255	986	1277	40
40*	59.1	0.9	2720	1118	1507	1067	1415	1032	1355	48
40**	24	36	2660	996	1293	997	1296	999	1298	50.5
45**	22	33	2710	975	1258	985	1275	992	1287	57
40**	59.1	0.9	2720	1059	1402	1034	1359	1017	1329	60
60*	39.4	0.6	2930	1025	1343	1015	1325	1007	1313	68
50**	30	20	2810	996	1268	989	1281	994	1291	72
80*	19.7	0.3	2860	943	1206	966	1243	982	1271	72
60**	24	18	2850	945	1208	967	1244	983	1272	83
60**	39.4	0.6	2930	975	1258	985	1275	993	1288	93
70**	24	6	2900	927	1179	955	1226	977	1262	98
80**	19.7	0.3	2860	901	1137	939	1199	968	1247	106

* CO contains 1.35 percent H₂O.

** CO contains 1.35 percent H₂O and 1.5 percent H₂.

* Six columns of T_i :—A: $E=30,000$, $T_i \sim 1000$; B: $E=30,000$, $T_i \sim 1300$; C: $E=50,000$, $T_i \sim 1000$; D: $E=50,000$, $T_i \sim 1300$; E: $E=100,000$, $T_i \sim 1000$; F: $E=100,000$, $T_i \sim 1300$. All temperatures are in °K, and activation energies, E , in cal. per g mole.

¹ C. Tanford and R. N. Pease, *J. Chem. Phys.* **15**, 431 (1947).

² G. Jahn, *Der Zundvorgang in Gasgemischen* (Oldenbourg, Berlin, 1942).

³ C. Tanford, *J. Chem. Phys.* **15**, 433 (1947).

⁴ C. Tanford and R. N. Pease, *J. Chem. Phys.* **15**, 861 (1947).

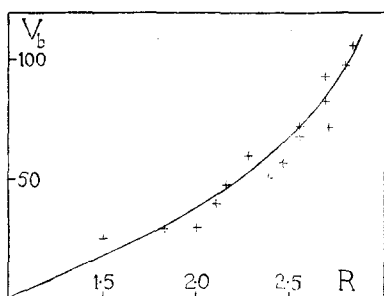


FIG. 1. Graph of the burning velocity, V_b , in cm/sec. against $R = (T_f - T_0)/(T_e - T_0)$ for moist carbon monoxide-oxygen flames.

percentage of oxygen being kept constant; (b) when the oxygen percentage is increased, the percentage of carbon monoxide being kept constant; (c) when hydrogen is added, the carbon monoxide and oxygen percentages being kept constant. The effect of (a) and (b) is to make the flame hotter and the effect of (c) is to increase the rate of reaction, i.e., the rate of heat release. Both would be expected to increase the flame speed according to a thermal theory.

Let us suppose that the reaction becomes thermally uncontrolled (i.e., explosive) at a temperature, T_e , when the rate of heat release reaches a value H . The value of H may be assumed to be a constant independent of composition because carbon monoxide, oxygen, and nitrogen have approximately the same heat capacities and thermal conductivities. On the basis of the kinetic results of Hadman, Thompson, and Hinshelwood⁵ (which have been interpreted in terms of a radical chain mechanism⁶) and because the rate of heat release is proportional to the rate of reaction, we may write

$$H = k \cdot \frac{p_{\text{CO}} \cdot p_{\text{H}_2\text{O}}}{p_{\text{O}_2}} \cdot e^{-E/RT_e} = k \cdot P \cdot e^{-E/RT_e}, \quad (1)$$

where

$$P = \frac{p_{\text{CO}} \cdot p_{\text{H}_2\text{O}}}{p_{\text{O}_2}},$$

where k is the transformation constant to convert reaction rate to rate of heat liberation and

⁵ G. Hadman, H. W. Thompson, and C. N. Hinshelwood, *Proc. Roy. Soc. A* **137**, 87 (1932).

⁶ C. N. Hinshelwood, *Kinetics of Chemical Change in Gaseous Systems* (Oxford University Press, London, 1933), p. 286; B. Lewis and G. von Elbe, *Combustion, Flames and Explosions in Gases* (Cambridge University Press, Teddington, England, 1938), p. 74.

involves the heat of reaction, E is the energy of activation, and H is that rate of heat release (assumed constant) at which the reaction just becomes explosive. We shall make the simplifying assumption in what follows that the effect of the added hydrogen is equal to that of an equivalent amount of water because the hydrogen will be rapidly converted to water. From (1) we may write

$$T_e = E/R(\log_e P - \log_e H'), \quad (2)$$

where $H' = H/k$ and is also a constant independent of composition. We have calculated the way in which T_e is expected to change with composition according to (2) for three values of E (30,000, 50,000 and 100,000 cal. per g mole) using for each value of E two values of the constant H' , one being chosen so that T_e is in the neighborhood of 1000°K, and the other so that T_e is in the neighborhood of 1300°K. These temperatures were chosen because they may be considered likely extremes for what is usually called the ignition temperature. The energy of activation is not likely to be greater than 100,000 or less than 30,000 cal. per g mole. The values of T_e calculated for the six combinations of E and H' are shown in Table I together with the compositions, the flame temperatures, T_f , given by Tanford and Pease, and the burning velocities of Jahn, V_b .

On a thermal conception of flame propagation we have to consider the time that will be taken in heating a portion of gas ahead of the flame up to the temperature, T_e , at which the reaction becomes thermally self-sustaining. This time will be longer the more closely $(T_e - T_0)$ (T_0 being the initial temperature) approaches $(T_f - T_0)$. So an increase in $(T_e - T_0)/(T_f - T_0)$ should lead to a decrease in V_b . Or, alternatively, V_b should increase as $(T_f - T_0)/(T_e - T_0)$ (represented by R) increases.⁷ In Fig. 1 V_b is plotted against R for E equal to 50,000 and H' selected so that T_e is about 1300°K or about 1000°C (middle of the range of values). It will be seen that all the points lie close to a smooth curve drawn through them. That is, V_b does increase in the fairly regular manner with R that is to be expected

⁷ Cf. Mallard and LeChatelier, *Ann. des. Mines* **4**, 274 (1883); also reference 6, p. 208.

from a thermal theory. The correlation between V_b and R obtained here is quite as satisfactory as that between V_b and p_H pointed out by Tanford and Pease.¹ Moreover, the correlation is also satisfactory for the other combinations of E and H' (rather better for E equal to 50,000 and T_e about 1000°K and for both values of T_e when E is 100,000; rather less good for both values of T_e (i.e., H') when E is 30,000). The interpretation is therefore hardly at all dependent on the exact values assumed for E and H' .

There is one point that may be added here. The line in Fig. 1 can reasonably be extrapolated

to pass through $V_b=0$, $R=1$, which is to be expected theoretically on the thermal theory since no flame could propagate if T_f were less than T_e , according to this theory.

Our general conclusion, therefore, is that the results of Jahn do not enable us to decide whether thermal conduction or radical diffusion is more important in the propagation of carbon monoxide-oxygen flames. We are, at the moment, carrying out determinations of burning velocities which we hope will help in deciding the relative importance of these two factors in the propagation of certain flames.

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Symmetry Matrices in Normal Coordinate Analysis

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A general symmetry matrix, U_n , has been derived which may be used to combine n equivalent coordinates in a molecule having the symmetry of any cyclic or dihedral point group of multiplicity n . The direct products $U_2 \times U_n$ and $U_2 \times U_2 \times U_n$ may be used in the cases of $2n$ and $4n$ equivalent coordinates. The symmetry type of each row of the symmetry matrices used has been determined.

THE secular equation necessary for a normal coordinate treatment of the vibrations of a molecule with N degrees of freedom may be represented by a polynomial equation of degree N , a determinantal equation of degree N or a matrix of order N . The superficial form of the secular equation varies with the choice of coordinates but the roots (which are simply related to the vibrational frequencies of the molecule) are independent of this choice. Wilson¹ has given a very convenient method by which the secular equation can be set up in terms of any given set of coordinates.

A set of valence-bond and valence-angle increases is usually not the best choice of coordinates that can be made. The use instead of certain linear combinations of these elementary coordinates may lead to a considerably factored form of the secular equation. Just which combinations, if any, are suitable is dependent on the

symmetry of the molecule. This factorization decreases considerably the number of terms that need be calculated and replaces one equation of high degree with several of lower degree.

The choice of these linear combinations of elementary valence coordinates (symmetry coordinates) has frequently been left to the experience and intuition of the worker. Wilson¹ has given some rules which must be satisfied by a set of symmetry coordinates. Venkatarayudu² has given a method for determining symmetry coordinates that is related to the method given in this paper. Eyring, Walter and Kimball³ have given a method which was derived for use with wave functions but may be applied to the problem of symmetry coordinates. In this method it is necessary to investigate the action of each of the symmetry operations of the point group appro-

² T. Venkatarayudu, *Proc. Ind. Acad. Sci.* **17a**, 50 (1943).

³ H. Eyring, J. Walter and G. Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York), Eq. (10.47), p. 189.

¹ E. Bright Wilson, Jr., *J. Chem. Phys.* **9**, 97 (1941).