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Calculations of Burning Velocities for Hydrogen–Bromine and Hydrogen–Chlorine Flames

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The effectiveness of certain of the simpler equations based upon various theories of burning velocity has been tested by calculating burning velocities for hydrogen–bromine and hydrogen–chlorine mixtures from independent kinetic data, without the use of any empirical factor. The equations developed by Semenov, Frank-Kamenetsky, and others, by Tanford and Pease, and by Manson were used. The last does not give good agreement with experimental data. The other two both give good agreement insofar as the *variation* of burning velocity with composition is concerned, but uncertainties in the data used make the absolute values rather poor. The Tanford–Pease equation also gives good agreement with temperature effects. The Semenov equation is not so successful unless an arbitrary energy of activation is used.

In attempts to calculate burning velocities by theoretical equations, an empirical factor usually has to be introduced to account for the reaction rates involved because of the lack of kinetic data. The hydrogen–bromine system has been under investigation for some time because it is one for which the mechanism of reaction seems well-established and for which data on rate constants are available. It offers, therefore, a possibility for calculation of the burning velocity without an empirical factor.

Certain preliminary calculations have already been reported.[1,2] In this paper, the results of a more detailed analysis of this system are reported, along with calculations for the hydrogen–chlorine system.

The theoretical equations of Tanford and Pease, Semenov, Frank-Kamenetsky, *et al.*, and Manson[3] were used for comparison. These were chosen because they illustrate theories involving mechanisms of flame propagation based upon diffusion of active particles, upon thermal effects, and upon projection of active particles because of a pressure differential. The equations are also simple enough to be handled by ordinary methods of calculation. Hirschfelder and his co-workers[4] have in progress a "complete" calculation, but find extreme difficulties in handling the equations even for a relatively simple chain mechanism.

The data on hydrogen–bromine and hydrogen–chlorine flames are useful for further evidence on the applicability of these approximate equations to real systems, even though it must be recognized that the kinetic data are such that extrapolation to flame temperatures may well give values which do not correspond very accurately to the actual values in the real flames. Furthermore the calculations do illustrate the influence of various factors upon two simple reaction chains, one of which represents a low-temperature, low-speed flame and the other a high-temperature, high-speed one.

Methods of Calculation.—The data and methods used are summarized only very briefly here. Details of the calculations are available elsewhere.[5] The classical mechanism of reaction was used as a basis of approach

$$X_2 \overset{K}{\rightleftarrows} 2X$$

$$X + H_2 \xrightarrow{k_2} HX + H$$

$$H + X_2 \xrightarrow{k_3} HX + X$$

$$H + HX \xrightarrow{k_4} H_2 + X$$

The equilibrium constants were taken from Lewis and von Elbe[6] (based on the data of Gordon and Barnes). The various rate constants were evaluated as already described,[2] using appropriate equilibrium constants and the various kinetic data.[7] Values for the various steps are shown in Table I.

TABLE I

RATE CONSTANTS

	H_2–Br_2	H_2–Cl_2
k_2 (cc./mole sec.)	$8.05 \times 10^{10}T$ $\times \exp - 17700/RT$	$6 \times 10^8 T \exp - 6000/RT$
k_3 (cc./mole sec.)	$2.59 \times 10^{11}T$ $\times \exp - 1100/RT$	$10^9 T \exp - 3000/RT$
k_4 (cc./mole sec.)	$3.08 \times 10^{10}T$ $\times \exp - 1100/RT$	$10^8 T \exp - 5000/RT$

The theoretical flame temperatures were evaluated for the adiabatic reaction.[1] Concentrations of the active particles were calculated for steady state conditions.[2] Calculations were made both for constant volume and constant pressure. The actual flames approach constant pressure; but, since the adjustment for expansion involves dissociation of the halogen, the slowest reaction in the series, the actual flames probably correspond to something between constant-pressure and constant-volume values. Typical calculated values are given in Table II.

Densities, heat capacities and viscosities for the various mixtures were calculated from the mole ra-

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(1) H. R. Garrison, Jas. A. Lasater and R. C. Anderson, 3rd Symposium on Combustion, Williams and Wilkins Co., Baltimore, 1949, p. 155.

(2) S. D. Cooley and R. C. Anderson, *Ind. Eng. Chem.*, **44**, 1402 (1952).

(3) C. Tanford and R. N. Pease, *J. Chem. Phys.*, **15**, 861 (1947); N. Manson, *ibid.*, **17**, 837 (1949); G. Markstein and N. Polanyi, Bumblebee Series Rept., No. 61 (Appl. Phys. Lab., Johns Hopkins); *cf.* also review by M. Evans, *Chem. Revs.*, **51**, 63 (1952).

(4) *Cf.* E. S. Campbell, D. R. Hughes and R. J. Buehler, "Equations for a Hydrogen-Bromine Flame: Computational Methods and Techniques," Univ. of Wis. Rept. No. CF-2109, Oct. 1953; Univ. of Wis. Naval Res. Lab., Madison, Wis.

(5) See the following series of unclassified reports of the Def. Res. Lab., Univ. of Texas (under sponsorship of Appl. Phys. Lab., Johns Hopkins Univ.): DRL-166 (May, 1948); DRL-219 (Sept., 1949); DRL-220 (Sept., 1949); DRL-227 (Sept., 1949); DRL-241 (March, 1950); DRL-257 (Aug., 1950); DRL-317 (March, 1953); DRL-318 (March, 1953); DRL-322 (March, 1953); DRL-323 (April, 1953).

(6) B. Lewis and G. von Elbe, "Combustion, Flames and Explosions of Gases," Academic Press, Inc., New York, N. Y., 1952.

(7) M. Bodenstein and G. Jung, *Z. physik. Chem.*, **121**, 127 (1926); J. C. Morris and R. N. Pease, THIS JOURNAL, **61**, 396 (1939); J. C. Potts and G. K. Rollefson, *ibid.*, **57**, 1027 (1925).

TABLE II

MAXIMUM PARTIAL PRESSURES OF ATOMS IN BURNING MIXTURES

	Constant vol.		Constant pressure	
% X_2	max p_x	max p_H	max. p_x	max. p_H
H_2–Br_2				
40	0.012	1.8×10^{-5}	0.023	3.7×10^{-5}
50	.024	8.4×10^{-6}	.042	1.8×10^{-5}
H_2–Cl_2				
40	.010	1.2×10^{-2}	.020	2.5×10^{-2}
50	.052	0.7×10^{-2}	.080	1.8×10^{-2}

tios and the values for the pure components. Heat conductivities were calculated from the viscosities and heat capacities, using the relationship for a perfect gas.[8] Specific data for a typical mixture are shown in Table III.

TABLE III

THERMAL AND DIFFUSION PROPERTIES

	T_f, °K.	$\bar{c}_p$, cal./g. °K.	Av. λ, cal./cm. °K. sec.	E, cal./g. mole	D_H, cm.²/sec.	D_X, cm.²/sec.
40% Br_2	1470	0.12	2.7×10^{-5}	40,310	0.97	0.11
40% Cl_2	2410	.28	8.6×10^{-5}	20,500	1.04	.19

The square-root law of Tanford and Pease was used in the usual form.[3] The values of k_H and k_X were determined from the sequence of reactions to be expected for the hydrogen and halogen atoms.[2] The equation of Manson[3] was also used directly. The equation of Semenov and Frank-Kamenetsky[3] was modified for application to a reaction of 1,5 order, corresponding to a rate expression of the type

$$\frac{d[HX]}{dt} \propto [H_2][X_2]^{1/2}$$

An expression for k at various concentrations of X_2 and HX could be evaluated from the kinetics of the reaction. The final equation for the burning velocity for mixtures with excess hydrogen was

$$S_T = \sqrt{\frac{2\lambda k b_{eff} e^{-E/RT} R^{1.5} T_0^{0.5} T_f^{2.5}}{\rho_0 \bar{c}_p a_0^{0.5} E^{1.5} (T_f - T_0)^{1.5}}}$$

where

λ = heat conductance
$\bar{c}_p$ = specific heat at constant pressure and at the av. temp. $(T_f + T_0/2)$
T_f = theoretical flame temp.
T_0 = initial temp.
b_{eff} = concn. of H_2 in final combustion products, moles/cc.
a_0 = initial concn. of X_2 moles/cc.
ρ_0 = initial density

k and E are determined from

$$\frac{d[HX]}{dt} = \frac{2k_2(k_3/k_4)K_{X_2}^{1/2}\,[H_2][X_2]^{1/2}}{(k_3/k_4) + \frac{[HX]}{[X_2]}} = ke^{-E/RT}\,[H_2][X_2]^{1/2}$$

K is the equilibrium constant for dissociation of the halogen.

For equimolar mixtures, or those with excess halogen, a somewhat different equation must be used.

Results

In determining the concentrations of free atoms in the system, it was noted[2] that, for the low temperature hydrogen–bromine system, maximum concentrations occurred at 90–95% reaction and there was a rather sharp decrease in the last stages of reaction. For the hydrogen–chlorine system, the effect of increasing temperature as reaction progressed became predominant, and maximum atomic concentrations occur at 100% reaction.

The flame temperature and equilibrium concentrations obtained here agree with those reported by Bartholome for hydrogen–chlorine system,[9] except that the concentration of hydrogen atoms calculated here is around three times as great as his.

Values of the burning velocity obtained from the various equations are summarized in Tables IV and V. The observed burning velocities are taken from the data of Bartholome[9] for the hydrogen–chlorine flames and Cooley, Lasater and Anderson[10] for the hydrogen–bromine. Table IV shows the results obtained with the Manson and Tanford–Pease equations when the effects of hydrogen atoms alone (u_H and V_H) and of halogen atoms alone (u_X and V_X) are considered in contrast to their combined effects. For the diffusion mechanism, the slow-diffusing and slow-reacting bromine atoms are essentially negligible in comparison with hydrogen atoms; but the lighter, more reactive chlorine atoms do have to be taken into account. In Table V, therefore, values of u_H were used for the hydrogen–bromine system and u_{tot} for the hydrogen–chlorine.

TABLE IV

EFFECTIVENESS OF HYDROGEN AND HALOGEN ATOMS

Mole	Tanford–Pease			Manson		
% X_2	u_H	u_X	u_{tot}	V_H	V_X	V_{tot}
40% Br_2	125	10	126	14	364	378
40% Cl_2	5090	1110	5220	286	256	542
50% Br_2	87	17	89	8	420	428
50% Cl_2	4010	1860	4420	181	492	673

TABLE V

BURNING VELOCITIES

	Tanford–Pease				
Mole % X_2	Const. vol.	Const. press.	Semenov, *et al.*	Manson	Exp.
		H_2–Br_2			
30	70	87	5	127	No flame
40	125	179	16	378	28
43	138	190	17		26
50	87	127	15	428	12
		H_2–Cl_2			
30	1790		617	204	
35					360
40	5210	7450	1018	542	405
43	5760	10900	934		
48	5230	7970	531	645	
50	4420	7010		673	350

The results in Tables IV and V show that the Manson equation, which does not take into account differences of reactivity in the particles, becomes overweighted in terms of the halogen atoms and does not, therefore, explain successfully the observed variations of burning velocity with composition.

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(8) *Cf.* J. H. Jeans, "Kinetic Theory of Gases," Cambridge Press, New York, N. Y., 1946, p. 187.

(9) E. Bartholome, *Z. Elektrochem.*, **54**, 169 (1950).

(10) S. D. Cooley, J. A. Lasater and R. C. Anderson, THIS JOURNAL, **74**, 739 (1952).

Both of the other equations are successful in predicting the type of variation of burning velocity with composition. If an empirical correction factor were used, each could give good agreement with experimental data. (The variation from the order of observed values at 40 and 43% is not serious since there is a question in the experimental data as to whether the maximum is at 40 or 42–44%).

The absolute values are not, however, in good agreement. These calculations show deviations similar to but somewhat greater than that reported by Clingman, Brokaw and Pease[11] for the methane–oxygen system. They are also similar to those found for the Semenov equation by Gerstein, McDonald, and Schalla for the ethylene oxide flame.[12] In each case, uncertainties in the data are sufficient to explain the deviations.

For the Tanford–Pease equation, there are obvious problems in extrapolating a relation such as that for k_3 to temperatures above 500°K. Possible errors in the energies of activation can cause wide variations in the calculated values. Pease[13] suggests, for example, the equation

$$k_2 = 4.56 \times 10^{12} T^{0.5} \exp - 18{,}780/RT$$

The ordinary form of the Tanford–Pease equation is based on average values for the various quantities. When, instead of using averages, the various quantities were determined for the various stages of reaction and the result integrated across the reaction line, the calculated burning velocities (constant-volume basis) for 43% bromine and 43% chlorine became 65 cm./sec. and 1523 cm./sec. (*cf.* Table V). Thus modification of the rate constants and method of calculation could readily give values in agreement with the experimental data.

For the equation of Semenov and Frank-Kamenetsky, there are, similarly, uncertainties in the kinetic data and in the heat conductances used.

Temperature Effect.—For the hydrogen–bromine reaction, calculations from these two equations can also be compared with observed burning velocities for different initial temperatures.[2] The treatment used was similar to that of Fenn and Calcote,[14] who found that the Semenov equation could be used to determine activation energies from observed temperature relations for hydrocarbon flames but that the Tanford–Pease equation could not be used since the temperature dependence of some of the terms was not known. For the hydrogen–bromine reaction, as already noted,[2] the temperature coefficient is low. The equation of Semenov, *et al.*, can be used to get the proper variation with temperature, but only by adjusting the energy of activation to 18–20 kcal./mole—an unreasonable value in terms of any available kinetic data. The Tanford–Pease equation can be used equally effectively in this case, where the temperature effect on p_H as well as k_H can be taken into account. The energy of activation is indicated to be in the range of 0–3 kcal./mole, which is within a reasonable range of the kinetic data.

Thermal *versus* Diffusional Effects.—Calculations of temperature and concentration gradients outside a theoretical flame front were also made, using a method similar to that of Tanford.[15] At a point corresponding to the mid-point of the reaction zone, the rate of reaction calculated on the basis of the increased temperature involved was less than one-tenth of that to be expected on the basis of the atomic hydrogen concentration resulting from diffusion. Thus an equation which places major emphasis on diffusion effects, particularly of atomic hydrogen, can be expected to work well in this case.

It is, however, of interest to note that, in deriving the Semenov-type equation, the assumption is made that $\lambda/\rho_0 c_p = D$. The term $ke^{-E/RT}$ is based upon the rate expression

$$\frac{d[HBr]}{dt} = ke^{-E/RT} = \frac{2k_2(k_3/k_4)K^{1/2}[H_2][Br_2]^{1/2}}{k_3/k_4 + k_4\dfrac{[HBr]}{[Br_2]}}$$

$$= \frac{2k_2k_3[H_2][Br][Br_2]}{k_3[Br_2] + k_4[HBr]}$$

The terms involving E, T_f and T_0 are included in effect as a basis for accounting for the variations in reaction over the range of temperatures in the flame. The Tanford–Pease equation on the other hand uses the diffusion coefficient of a particular active particle such as the hydrogen atom and sums up the rate effect by integration, over the temperature range, of $k_H p_H [Br_2]$. But

$$k_H = 2k_3$$

and pH is determined from

$$\frac{k_2[Br][H_2]}{k_3[Br_2] + k_4[HBr]}$$

Thus one equation uses in effect a general diffusion coefficient for the mixture, the other a coefficient for a specific particle. Both use essentially the same rate factors but treat them in somewhat different fashion. They represent two approaches to burning velocity which are analogous to the two possibilities of expression of the rate of a series of reactions in terms of one or two rate-determining steps or in terms of a general summation or averaging of steps.

Either or both might be applied in empirical correlations by use of appropriate correction factors. In theoretical calculations the question of which is best would depend upon the extent to which a particular particle or particles might be predominant in determining properties of the individual system in question.

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[11] W. H. Clingman, R. S. Brokaw and R. N. Pease, "4th Symposium on Combustion," Williams and Wilkins Co., Baltimore, 1953, p. 310.

[12] M. Gerstein, G. E. McDonald and R. Schalla, *ibid.*, p. 375.

[13] R. N. Pease, "Equilibrium and Kinetics of Gas-Phase Reactions," Princeton Press, Princeton, N. J., 1942, p. 119.

[14] J. B. Fenn and H. F. Calcote, "4th Symposium on Combustion," Williams and Wilkins Co., Baltimore, 1953, p. 231.

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