

THE FIRST LIMIT OF THE HYDROGEN + OXYGEN REACTION IN POTASSIUM CHLORIDE-COATED VESSELS

By R. R. BALDWIN

Chemistry Dept., The University, Hull

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The treatment described in the preceding paper is applied to the first limit of the hydrogen + oxygen reaction in KCl-coated vessels. The results show that the surface destruction of hydrogen atoms can be only moderately efficient, and that surface destruction of either oxygen atoms or hydroxyl radicals also occurs. For a wide range of mixture compositions, the observed limits can be predicted with a r.m.s. deviation *ca.* 1 % for a range of temperatures and vessel diameters. From the constants obtained, the rate constants of the reaction $\text{H} + \text{O}_2 = \text{OH} + \text{O}$, and of oxygen atoms or hydroxyl radicals with hydrogen can be deduced. Some consequences to the mechanism of the hydrogen + oxygen reaction are also discussed.

Although the second limit of the hydrogen + oxygen reaction has been thoroughly investigated by a number of workers, relatively few studies of the first limit have been made. Moreover, most workers¹⁻⁶ have been concerned with establishing the main qualitative features, and have not attempted a precise quantitative treatment. In some cases, this has probably been due to the difficulty of obtaining continuously reproducible results with the particular surface employed. Where a precise treatment has been attempted,^{5,6} it is doubtful whether the reproducibility of the results is sufficient to permit a detailed analysis.

The marked reduction in the rate of oxidation of hydrogen,⁷ ethane,⁸ propane⁹ and other hydrocarbons¹⁰ obtained by coating the vessel surface with KCl has led to the tacit assumption that KCl is an efficient surface for the destruction of all chain centres. Thus, in assessing the effect of surface termination on the second limit, Lewis and von Elbe¹¹ imply that hydrogen atoms are efficiently destroyed at a KCl surface. Direct measurements by Smith¹² of the heat of

recombination of hydrogen atoms on various surfaces show, however, that KCl is relatively inefficient up to 400° C. Moreover, Warren¹³ has used measurements of the first limit to compare the efficiency of various surfaces for hydrogen atoms by writing the surface destruction constant k_H equal to A/P . The value of A obtained for KCl is about one-tenth of the value for surfaces such as KOH, Al_2O_3 and PbO. From the discussion in the preceding paper,¹⁴ it is clear, as admitted by Warren, that this treatment can be only approximate, and that the apparent value of A for KCl will depend on the pressure involved.

The present study of first limits in KCl-coated vessels was made primarily to assist work on the inhibition of the second limit of the hydrogen + oxygen reaction by hydrocarbons.^{15, 16} Studies in a range of vessels from 14 to 36 mm diam. suggested that the apparent variation in the effectiveness of inhibition with vessel diameter could be attributed to surface destruction of hydrogen atoms, and of oxygen atoms or hydroxyl radicals, rather than to any diameter dependent process in the actual inhibition. To confirm this by making the necessary corrections for such surface termination required a knowledge of the surface destruction constants over a range of pressures, and the present work was undertaken with this end in view.

EXPERIMENTAL

The apparatus used for this work has already been described.¹⁵ The first limit was determined by observation of the flash occurring when a known pressure of the mixture was expanded into the evacuated reaction vessel, the expansion ratio having been previously determined. By carefully excluding light from the front end of the furnace, and using a black cloth at the window end, the flashes could be detected with reasonable ease. Approach from the explosive or non-explosive side did not appear to affect the resultant limit, but as a precaution the limit was normally approached from the explosive side. Between successive experiments, the reaction vessel was pumped out, rinsed with hydrogen, and evacuated for 3 min before the next admission.

As in the inhibition studies, it was found convenient to vary the hydrogen and oxygen mole fractions independently. For this reason a "standard" mixture of high nitrogen content was selected, containing 0.28, 0.14 and 0.58 mole fractions of hydrogen (x), oxygen (y), and nitrogen respectively. Variation in hydrogen and oxygen mole fractions independently could thus be made by interchanging hydrogen or oxygen respectively with nitrogen. A particular advantage of this procedure is that a wide range of oxygen mole fractions can be studied without large variations in the diffusion constants of the radicals involved. In addition to the above two series, the effect of hydrogen was investigated in mixtures with a constant high oxygen mole fraction of 0.56.

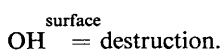
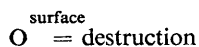
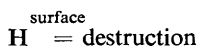
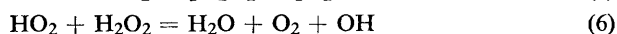
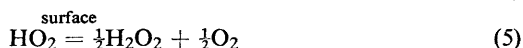
To ensure consistency of surface conditions for all the mixtures examined, the majority of the limits for a given vessel at a given temperature were obtained in one day. Determination of the first limit of the "standard" mixture was made at the beginning, in the middle, and at the end of each day, and if the variation exceed $\pm 1\%$, the results were rejected. It was normally possible to study two series in one day, and to complete the third (the variation of x with $y = 0.14$) on the following day.

It was found that the first limit of the standard mixture was particularly low with a fresh KCl surface, and that the limit gradually rose as the surface aged, tending toward a fairly constant value. The majority of the measurements were carried out on such an aged surface, as with the fresh surface the limit changed appreciably during a single day.

The experimental accuracy was limited by three main factors. The low pressures could be measured by the Bourdon gauge to within $\frac{1}{4}\%$ in most cases, although with the smaller pressures involved at the higher oxygen mole fractions in the largest vessels, the error could amount to $\frac{1}{2}\%$. With most mixtures ($y < 0.28$), the sharp extinction of a red flash permitted the explosion boundary to be located to within $\frac{1}{4}\%$. This error increased to about $\frac{1}{2}\%$ with the higher oxygen mole fractions, as the flash was whitish near the boundary and detection of its extinction was more difficult. The reproducibility of the surface was the most serious source of error, despite frequent checks with the standard mixture. Under favourable conditions the probable error is about $\frac{1}{2}\%$, but in unfavourable circumstances, this might increase to 1%. In general, the overall accuracy of determination for the lower oxygen mole fractions is $\frac{1}{2}$ -1%, and at the higher oxygen mole fractions 1-2%, the figure depending largely on the surface reproducibility.

MECHANISM OF THE FIRST LIMIT

To present and discuss the results, a specific mechanism must be adopted for the first limit. All workers are agreed on the occurrence of reactions (1)-(3), and although the gas phase termination reaction (4) is relatively small at the first limit, and has been ignored by most other workers, it does make some contribution and must be included in an exact treatment. It can then be assumed that the HO_2 radicals are completely destroyed at the surface by reaction (5a), or the reactions (5) and (6) suggested by Lewis and von Elbe^{17, 18} can be employed.



The combination of reactions (1)-(6) together with the efficient destruction of hydrogen atoms at the surface would cause the first limit to decrease continuously as the hydrogen mole fraction was decreased at constant oxygen mole fraction. This decrease would arise partly from the reduction in the third-body coefficient for reaction (4) as the hydrogen content is reduced, and partly from the reduction in diffusion coefficient. Experimentally, as seen from table 1, the limit rises at low hydrogen mole fraction, and this can only be attributed to the surface destruction of a chain centre which has an alternative reaction with hydrogen giving chain propagation or chain branching. Since both oxygen atoms and hydroxyl radicals react with hydrogen, this second surface termination process is not uniquely defined. Most other workers have selected one or the other with little attempt to justify their choice.

Considering all feasible reactions, four possibilities may be examined.

A. SIMPLE MECHANISM, OH DESTROYED AT SURFACE

Taking reactions (1)-(4), (5a) and surface destruction of H and OH, stationary state treatment gives the explosion boundary as

$$\frac{k_{\text{H}}}{2k_2[\text{O}_2]} + \frac{k_{\text{OH}}}{k_1[\text{H}_2] + k_{\text{OH}}} = 1 - \frac{P_1}{P_2^\circ} \quad (i)$$

$P_2^\circ = 2k_2/k_4$ is the second limit in the absence of surface termination of H and OH. This can be estimated with sufficient accuracy from experimental measurements of the second limit.

B. COMPLEX MECHANISM, OH DESTROYED AT SURFACE

If reaction (5a) is replaced by (5) and (6), eqn. (i) is modified to

$$\frac{k_{\text{H}}}{2k_2[\text{O}_2]} + \frac{k_{\text{OH}}(1 + P_1/2P_2^\circ)}{k_1[\text{H}_2] + k_{\text{OH}}} = 1 - \frac{P_1}{P_2^\circ} \quad (ii)$$

where P_2° is now given by $3k_2/k_4$. The term $P_1/2P_2^\circ$ arises from the increased

OH concentration resulting from reactions (5) and (6). The difference between (i) and (ii) is barely significant, since under conditions where P_1/P_2° is appreciable, the contribution of the k_{OH} term is relatively unimportant.

C, D. OXYGEN ATOMS DESTROYED AT SURFACE

With both simple and complex mechanisms, the explosion boundary condition is identical with (i) except that k_{OH} , k_1 are replaced by k_O , k_3 respectively.

The choice between these four possibilities is governed firstly by the adoption of either (5) or (5a), and secondly by the relative values of k_{OH}/k_1 and k_O/k_3 . It is considered that present evidence slightly favours the more complex mechanism of Lewis and von Elbe, involving reactions (5) and (6). Smith¹² has given evidence that hydroxyl radicals are efficiently destroyed at a KCl-coated surface, while the published value for k_1 ^{19, 20, 21} is significantly less than that for k_3 .^{19, 20} For this reason surface destruction of OH was originally adopted in discussing the first limit measurements. A closer examination, however, shows that this evidence cannot be considered conclusive. The rather dogmatic statements of the value for k_3 appear to be derived from some early work by Harteck and Kopsch,²² in which a collision yield of 10^{-7} at room temperature and an activation energy of 6 kcal are quoted. The values quoted for k_3 ,^{21, 22} however, give a normal steric factor with this activation energy, and this is not consistent with the above collision yield at room temperature. Either the steric factor must be *ca.* 10^{-3} with $E_3 = 6$ kcal, or if the steric factor is unity, then E_3 must be about 10 kcal. The first possibility makes reaction (3) slower at 500° C than the value reported for (1), and in fact slower than recent estimates^{15, 16} of (2). The second possibility makes reactions (1) and (3) of comparable speed at 500° C. Moreover, recent work using microwave absorption to detect the OH radical²³ has cast doubt on the conclusion of Smith that OH radicals are efficiently destroyed at a KCl surface. In addition, observations by Linnett and Marsden²⁴ have shown that although oxygen atoms are not destroyed very efficiently on a KCl surface at room temperature, the destruction becomes quite efficient at 400° C. It appears that the situation is sufficiently confused for no choice to be made between destruction of OH and O from available evidence, and eqn. (ii) given by case B has, therefore, been retained for discussing the present results. In any case, calculations show that the use of the alternative eqn. (i) given by cases A, C and D give results which are effectively identical with those obtained from (ii).

RESULTS

Two observations during the present work confirm that KCl is relatively inefficient for the destruction of hydrogen atoms. In the first place, the limit obtained depends to some extent on the previous history of the surface, tending to increase as the surface is aged. Thus, with a particular mixture at 520° in a 51 mm diam. vessel, the first limit was 4.90 mm Hg for the freshly coated surface, rising to 8.41 mm after the vessel had been in use about two weeks. Such a rise in the limit is hardly feasible if the surface was originally efficient. Secondly, even with the aged surface, it has been found impossible to interpret the results of first limit measurements on the assumption that hydrogen atoms are efficiently destroyed, whereas a precise interpretation is possible using the treatment for surfaces of intermediate efficiency which has been described in the preceding paper.¹⁴

If it is assumed that both surface destruction constants are inversely proportional to pressure (efficient destruction), it is convenient to write

$$\frac{k_H}{2k_2} = \frac{aA}{P} \quad \frac{k_{OH}}{k_1} = \frac{cC}{P}, \quad (\text{iii})$$

where, for a cylinder of radius r ,

$$\begin{aligned} A &= (2.405)^2 D_H^2 / 2k_2 r^2, \\ C &= (2.405)^2 D_{OH}^2 / k_1 r^2. \end{aligned} \quad (\text{iv})$$

a and c are coefficients allowing for the variation of diffusion coefficient with mixture composition. For convenience in calculation, a and c are expressed with respect to the standard mixture as unity, so that D_{H}° , D_{OH}° are the diffusion coefficients of hydrogen atoms and hydroxyl radicals through the "standard" mixture at unit pressure. In calculating the values of a and c given in table 1, the formula used by Melville²⁵ for diffusion in a mixture of gases has been adopted:

$$1/D = P_{\text{A}}/D_{\text{A}} + P_{\text{B}}/D_{\text{B}} + P_{\text{C}}/D_{\text{C}},$$

or

$$1/D = P(x_{\text{A}}/D_{\text{A}}^{\circ} + x_{\text{B}}/D_{\text{B}}^{\circ} + x_{\text{C}}/D_{\text{C}}^{\circ}), \quad (\text{v})$$

where x is the mole fraction, and D° the diffusion coefficient at unit pressure. The diffusion coefficients of hydrogen atoms and hydroxyl radicals through hydrogen, oxygen and nitrogen have been calculated using the Stefan-Maxwell relation.^{26, 27} The collision diameters used were those given by Kennard,²⁸ together with values of 2.74 and 3.00 Å for hydrogen atoms²⁹ and hydroxyl radicals. For hydrogen, oxygen and nitrogen, the ratios of the diffusion coefficients D_{H} and D_{OH} are 1.83:1.115:1 and 3.62:1.09:1 respectively.

Combining (ii) and (iii), and re-arranging,

$$\frac{aA}{y} = P_1^2 \left(1 - \frac{P_1}{P_2^{\circ}} \right) - \frac{cC(1 + P_1/2P_2^{\circ})}{(x + cC/P_1^2)}. \quad (\text{vi})$$

There is no simple graphical method of testing whether (vi) will satisfy the observed first limits for a range of mixture composition. If, however, the value of C derived later in this paper is assumed, the right-hand side of (vi) can be evaluated for each mixture. Denoting this by F , (vi) can be written:

$$aA/y = F,$$

so that a plot of F against a/y should give a straight line through the origin. In fact, a curved relation is obtained, but a value of A can be obtained by drawing a mean line through the origin. Eqn. (vi) can now be used to calculate the first limits of all mixtures examined. Table 1, which gives the observed and calculated results for a 51 mm diam. KCl-coated vessel at 500° C shows a r.m.s. deviation of 15 %, which cannot be improved by altering the value of C . This compares with a value of 0.7 % obtained when the same results are treated by the method developed for a surface of intermediate efficiency. It is clear, therefore, that even an aged KCl surface cannot be regarded as completely efficient for the destruction of hydrogen atoms at first limit pressures.

TABLE 1.—AGREEMENT OF OBSERVED AND CALCULATED FIRST LIMITS

x	y	diffusion constants		$P_1 \text{ obs.}$	calc. limit	
		a	c		A	B
0.28	0.72	1.076	1.063	3.49	4.50	3.48
	0.56	1.053	1.045	3.99	4.98	3.96
	0.28	1.017	1.015	6.02	6.73	5.96
	0.14	1.000	1.000	9.78	9.39	9.76
	0.10	0.994	0.996	12.58	11.22	12.69
	0.07	0.991	0.993	16.92	13.85	17.17
0.86	0.14	1.441	2.146	—	—	—
0.56		1.174	1.347	10.23	10.25	10.26
0.28		1.000	1.000	9.78	9.39	9.76
0.14		0.931	0.886	10.03	9.01	9.99
0.10		0.913	0.858	10.32	9.27	10.27
0.07		0.900	0.838	10.80	9.50	10.75
0.44	0.56	1.156	1.235	—	—	—
0.28		1.053	1.045	3.99	4.98	3.96
0.14		0.979	0.922	4.41	5.17	4.43
0.10		0.958	0.891	4.75	5.38	4.77
0.07		0.944	0.869	5.12	5.66	5.18

A , calculated on the assumption that hydrogen atoms are efficiently destroyed at the surface, using eqn. (vi) $C = 2.4$.

B , calculated assuming surface of moderate efficiency for H atoms, using eqn. (ix); values of A , B and C from table 3.

Using the expression developed in the preceding paper for cylindrical vessels with surfaces of intermediate efficiency, k_H is modified to

$$k_H = \frac{(2.405)^2 ja D_H^\circ / r^2}{P(1 + 2.75aB/P)} \quad (\text{vii})$$

$$\text{Hence} \quad \frac{k_H}{2k_2} = \frac{jaA}{P(1 + 2.75aB/P)} \quad (\text{viii})$$

where A is given by (iv), and j is a small correction factor * near unity, dependent on the value of aB/P . If, following Smith,¹² it is assumed that the destruction of OH on a KCl-coated surface is efficient, eqn. (iv) for k_{OH} is retained. With this modification, (vi) becomes

$$\frac{jaA}{y(1 + 2.75aB/P)} = P_1^2 \left(1 - \frac{P_1}{P_2^\circ} \right) - \frac{cC(1 + P_1/2P_2^\circ)}{(x + cC/P_1^2)} = F. \quad (\text{ix})$$

Eqn. (ix) can be re-arranged in the form,

$$\frac{yF}{aj} + \frac{2.75 ByF}{jP_1} = A. \quad (\text{x})$$

A plot of yF/aj against yF/jP_1 thus gives a straight line of gradient $2.75B$ and intercept A . Although in principle this permits the determination of the unknowns A and B , two difficulties arise. First, the value of C is not known initially, and second the value of B is required to obtain the values of j necessary to make the plot, since j is a known function of aB/P . The following procedure is, therefore, necessary.

(1) A value of C is assumed, and the quantity F calculated for all mixtures from the experimental first limits.

(2) A value of B is assumed, and the correction factor j calculated from the relevant values of aB/P_1 .

(3) The plot of yF/aj against yF/jP_1 is made. If the best straight line through the points gives a value of B different from that assumed, a more probable value of B must be taken and the calculations in (2) repeated. A series of successive approximations ensure that the correct values of A and B are obtained from the best straight lines through the points. In practice, since j always lies close to unity, only one such approximation is normally required.

TABLE 2.—COMPARISON OF OBSERVED AND CALCULATED FIRST LIMITS
Aged KCl-coated vessels at 520° C

diam. mm		51		36		24		14	
mole fraction		$P_{\text{obs.}}$	$P_{\text{calc.}}$	$P_{\text{obs.}}$	$P_{\text{calc.}}$	$P_{\text{obs.}}$	$P_{\text{calc.}}$	$P_{\text{obs.}}$	$P_{\text{calc.}}$
H ₂	O ₂								
0.28	0.72	3.28	3.24	4.16	4.13	5.16	5.25	10.15	10.22
	0.56	3.60	3.63	4.73	4.68	6.12	6.10	11.82	11.83
	0.28	5.61	5.58	7.11	7.06	9.63	9.46	19.78	19.54
	0.14	9.07	9.10	11.50	11.55	16.30	16.26	27.74	27.24
	0.10	11.72	11.75	15.08	15.14	22.01	22.14	43.16	43.72
	0.07	15.49	15.56	21.15	20.81	33.53	33.64	—	—
0.86	0.14	—	—	12.89	13.01	—	—	—	—
0.56		9.30	9.38	12.00	12.01	17.06	17.08	—	—
0.28		9.07	9.10	11.50	11.55	16.30	16.26	—	—
0.14		9.42	9.35	11.90	11.90	16.78	16.68	—	—
0.10		9.72	9.60	12.20	12.21	17.61	17.35	—	—
0.07		10.11	9.98	12.78	12.77	18.45	18.16	—	—
0.44	0.56	—	—	4.43	4.42	5.66	5.71	11.11	11.23
0.28		3.60	3.63	4.73	4.68	6.12	6.10	11.82	11.83
0.14		4.12	4.12	5.27	5.27	7.02	6.98	13.39	13.46
0.10		4.33	4.37	5.62	5.65	7.44	7.49	14.67	14.68
0.07		4.68	4.74	6.00	6.10	7.99	8.12	15.99	15.97
r.m.s. deviation		0.8 %		0.8 %		1.0 %		1.0 %	

* j is used for convenience to replace j'' in the preceding paper.

(4) If the wrong value of C has been assumed, the points for varying hydrogen mole fractions (at constant oxygen mole fractions of 0.14 and 0.56) lie in a skew manner across the mean line. A new value of C is selected, and the whole process repeated until this skew feature has been eliminated.

(5) While obviously incorrect values of C can be detected by the graphical scatter introduced, the best value of C is most conveniently selected by using eqn. (ix) to calculate the first limits of all mixtures, using the relevant values of A and B for each value of C selected. The combination giving the least r.m.s. deviation is then selected. In some cases, this procedure weighted unduly the less accurate points obtained by varying x with $y = 0.56$. A compromise was then adopted between these values of A , B and C , and those giving the best agreement for the more accurate measurements with variable hydrogen mole fraction at $y = 0.14$.

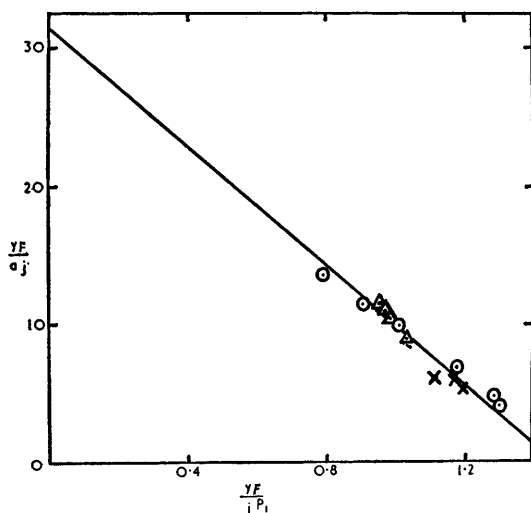


FIG. 1.—Plot of yF/aj against yF/jP_1 .

51 mm diam. KCl-coated vessel
at 500° C; $C = 2.4$.

○ y variable, $x = 0.28$;

△ x variable, $y = 0.14$;

× x variable, $y = 0.56$.

Fig. 1 indicates a typical plot obtained with the experimental results from table 1 when the best value of C (2.4) is used. It should be noted that the plot is quite sensitive to experimental error, and that the r.m.s. deviation of the calculated limits is only 0.7%. Table 2 shows the comparison of observed and calculated limits for four vessel diameters at 520° C. In all cases, the r.m.s. deviation is within 1%. Similar agreement was obtained over the temperature range 500–550° C. This success in the application of eqn. (ix) confirms the accuracy of the treatment developed for such intermediate surface efficiencies.

The values of A and C for a series of vessels over a range of temperatures are summarized in table 3. The values of B are also included, but no significant trends are to be expected here, since the value obtained depends markedly on the pre-treatment of the vessel surface.

TABLE 3.—SUMMARY OF SURFACE DESTRUCTION CONSTANTS

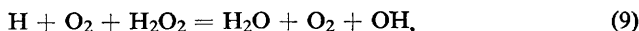
vessel diam. (mm)	temp. °C	A	B	C	Ad^2 $\times 10^{-3}$	Cd^2 $\times 10^{-3}$
36	550	42.5	10.8	3.25	55	4.2
36	540	45.5	11.3	3.2	58	4.1
24		111	20.0	5.5	63	3.2
14		335	35.0	18.0	66	3.5
51	520	30.3	7.5	1.9	79	4.9
36		51	10.8	3.45	66	4.5
24		132	23.0	6.0	76	3.5
14		403	37.0	18.0	79	3.5
51	500	31.5	7.8	2.4	82	6.2
36		61.0	12.3	3.7	79	4.8

DISCUSSION

In assessing the results shown in table 3, the accuracy with which the constants A , B and C can be determined must first be examined. The values of A and B are effectively determined from the variation of F over a pressure range, i.e. from the series in which the oxygen mole fraction is varied from 0.07 to 0.72. Moreover, the values of A and B are interdependent since the same value of k_H at a given pressure can be obtained with either low values of both A and B , or with high values of both. Further, changing from low values of A and B to high values produces a relatively small change in the variation of k_H with pressure. The destruction of hydroxyl radicals is a relatively minor process, so that the constant C can only be determined to about 10 %. Nevertheless, the term involving C , though relatively small, does become important at high oxygen mole fractions and thus its value affects the variation of F with pressure. As a result of this interlocking of the three constants, it is only possible to determine A and B to about 10 %.

Within these limitations, table 3 shows that A and C are both inversely proportional to the square of the vessel diameter, as required by (iv). For a given vessel over a range of temperatures, the plots of $\log A$ and $\log C$ against $1/T$, after correction for the conversion of pressure to concentration, give activation energies of 15.2 and 9.2 kcal respectively. While it is not suggested that the present determinations of A and C are sufficiently reliable to enable accurate evaluation of the activation energies of reactions (2) and (1), the agreement with the accepted activation energies¹⁹ provides further evidence that the treatment developed is satisfactory. Further work with more efficient surfaces, where the constant B is less important, may permit a more precise evaluation of A and C , and of their variation with temperature.

Some assumptions made in the treatment may be briefly examined. The assumption that the relatively small gas phase termination can be allowed for by the factor P_1/P_2° in eqn. (ix) is correct if reaction (5a) occurs, or if reactions (5) and (6) occur at all pressures. Lewis and von Elbe,¹¹ however, have attributed the decrease in the second limit in small vessels to the fact that reaction (9)



predominates over reaction (6) in these small vessels.

This reaction should also predominate at low pressures, in which case the gas phase termination factor becomes $3P_1/2P_2^\circ$. Since P_1/P_2° rises to about 0.4 with low oxygen mole fraction in the small vessels, such a modification in eqn. (ix) should be easily detected. The absence of any discrepancies between observed and calculated values in such cases suggests that eqn. (ix) has the correct allowance for gas phase termination. This confirms the conclusion, drawn later, that reaction (9) either does not occur, or is of negligible importance.

The choice of reactions (5) and (6) instead of (5a) introduces the factor $P_1/2P_2^\circ$ into the last term of (ii) and (ix). This factor is normally quite small, and under conditions where it becomes significant, the contribution of the last term is in any case relatively unimportant. Calculations on one set of results using eqn. (i) instead of (ii) showed that the values of A and of the root-mean-square deviation were effectively unaltered, and that C was increased by less than 10 %.

A check on the relative values of the diffusion constants employed was provided by the mixture containing 0.86 mole fraction hydrogen, as the variation of a from unity is greatest in this case. The absence of any abnormal discrepancies between observed and calculated values confirms that the correct relative value for hydrogen has been used. Since the diffusion constants for H atoms in oxygen and nitrogen do not differ greatly, their relative values are unlikely to be in error. The only cases where the values of c might be in error are at high hydrogen mole fractions, and under such conditions the contribution of the C term is almost negligible.

In a number of cases, it was found that the value of C required to avoid any skew distribution with varying hydrogen at $y = 0.56$ was a little less than with $y = 0.14$. The possibility that this might arise from inefficiency in the destruction of hydroxyl radicals at the surface was eliminated by showing that use of a similar expression to (vii) for k_{OH} exaggerated this effect and increased the r.m.s. deviation. A possible contribution from surface destruction of O in addition to OH was also shown to be incapable of improving the r.m.s. deviation.

A limited number of tests were made with a relatively fresh and heavily coated 36 mm diam. vessel at 520° C. Experimental difficulties were slightly increased, partly because of the difficulty of detecting weak flashes through the KCl coating, and secondly because of the ease with which the surface changed. Using the same values of A and C (3.6) obtained for the aged vessel and merely modifying B , it was possible to predict the limits with a r.m.s. deviation of 1.8 %. By changing C to 4.4, this could be reduced to a minimum of 0.9 %. The change is barely outside the errors in the determination of C , and the agreement provides further confirmation that the hydroxyl radical (or oxygen atom) destruction is effectively diffusion controlled.

Surface destruction of hydroxyl radicals rather than oxygen atoms was selected for the reasons given earlier. This choice does not significantly affect the conclusions drawn in this paper, since the equations obtained are kinetically identical with (ii), apart from the term $P_1/2P_2$. It has already been noted that the omission of this term does not significantly affect the calculations. Moreover, the relative diffusion constants for oxygen atoms will be effectively identical with those calculated for hydroxyl radicals.

CONCLUSIONS

The validity of the treatment developed for surfaces of intermediate efficiency is shown by the precise prediction of first limits that is possible for a range of mixtures in KCl-coated vessels. Further confirmation is obtained by using the values of B to estimate the surface efficiency. From the first limit of 4.90 mm Hg at 520° for the standard mixture in the 51 mm diam. freshly coated vessel, $B = 19.7$. Taking λ_0 for H atoms in the standard mixture as *ca.* 2.5×10^{-2} cm, $\epsilon = 6.6 \times 10^{-4}$. This is consistent with the value of 2×10^{-4} at 400° C given by Smith,¹² the value increasing as the temperature rises. The corresponding limit for an aged vessel gives $B = 7.5$, $\epsilon = 1.7 \times 10^{-3}$.

From the experimental values of A and C , the absolute values of k_2 and k_1 (or k_3) can be evaluated using relation (iv). The diffusion constants are calculated from the expression $D_0 = \lambda_0 \bar{c}/3$, using the collision diameters already quoted. The results obtained at 520° C are:

$$k_1 \text{ (or } k_3) = 3.4 \times 10^{-14} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1},$$

$$k_2 = 4.5 \times 10^{-15} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}.$$

The value of k_2 is in reasonable agreement with the figure of 1.1×10^{-14} obtained by Semenoff³⁰ from measurements of the branching factor within the explosion peninsula. A further estimate of 1.1×10^{-15} has been obtained from a study of the inhibition of the second limit by ethane.^{15, 16} This value is dependent on an extrapolation of the data³¹ for $H + C_2H_6$ up to a temperature of 520° C, and may be in error by a factor of up to 10. All these values are significantly higher than the figure of 0.88×10^{-17} which can be calculated from the expression given by Lewis and von Elbe.¹⁸ Use of this latter value gives a rate constant k_4 which is lower by a factor of about 10^3 than the rate constants for the recombination of bromine atoms and chlorine atoms.³² Adoption of the higher value for k_2 , suggested above, would bring the velocity constant of reaction (4) into agreement with those for similar three-body reactions.³³

The only estimation of k_1 is that of Avramenko and Lorentzo²¹ in the range 105–216° C. Extrapolation of their formula to 520° C gives a value of 7×10^{-13} cm³ mole⁻¹ sec⁻¹. The discrepancy may arise either because C is determined by k_3 rather than k_1 , or because of the steric factor and activation energy selected by Avramenko and Lorentzo.²¹ Their experimental method has been criticized.³⁴ The uncertainty in previous estimations of k_3 has already been noted.

Lewis and von Elbe¹¹ find a variation in the second limit from 88 mm for $2\text{H}_2 + \text{O}_2$ in a 10 cm diam. spherical KCl-coated vessel at 530° C to 68 mm in a 1.8 cm vessel, and invoke a special mechanism involving reaction (9) to account for this variation. Using the values of A and C obtained in this paper, making allowance for the change from cylindrical to spherical shape, and making a suitable estimate of B , it can be shown that the limit should decrease about 10–12 mm as a result of surface termination in the smaller vessel. A further change will occur as the result of the occurrence of the regeneration reaction $\text{HO}_2 + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H}$ in the larger vessel. Using the data given by Lewis and von Elbe, it can be shown that this reaction will cause a minimum change of about 5 mm, and that it will have a greater effect if the surface destruction of HO_2 is not efficient. Observations³⁵ on the effect of thickness of KCl coating suggest that B/P for HO_2 is not negligible even at third limit pressures, and this term will become more important at second limit pressures. Most, if not all, of the observed diameter dependence of the second limit can thus be attributed to the combined effects of surface destruction and regeneration reactions, and the special reaction (9) proposed by Lewis and von Elbe must either be absent or have a relatively minor effect. Confirmation of this conclusion is provided by the fact, mentioned in the discussion, that the third body termination at the first limit is accounted for by the factor P_1/P_2° rather than $3P_1/2P_2^\circ$.

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¹ Semenova, *Acta Physicochim.*, 1937, **6**, 25.

² Biron and Nalbandjan, *Acta Physicochim.*, 1937, **6**, 43.

³ Hinshelwood and Moelwyn-Hughes, *Proc. Roy. Soc. A*, 1932, **138**, 311.

⁴ Garner and Willavoys, *Trans. Faraday Soc.*, 1935, **31**, 805.

⁵ Frost and Alyea, *J. Amer. Chem. Soc.*, 1933, **55**, 3227.

⁶ Voevodski, *Acta Physicochim.*, 1947, **22**, 45.

⁷ Pease, *J. Amer. Chem. Soc.*, 1930, **52**, 5106.

⁸ Taylor and Riblett, *J. Physic. Chem.*, 1931, **35**, 2667.

⁹ Pease, *Chem. Rev.*, 1937, **21**, 279.

¹⁰ Prettre, 3rd Symp. *Combustion, Flame and Explosion Phenomena* (Wisconsin, 1949).

¹¹ Lewis and von Elbe, *Flame, Combustion and Explosion Processes in Gases* (Academic Press, New York, 1951), p. 48.

¹² Smith, *J. Chem. Physics*, 1943, **11**, 110.

¹³ Warren, *Proc. Roy. Soc. A*, 1952, **211**, 86.

¹⁴ Baldwin, *Trans. Faraday Soc.*, 1956, **52**, 1337.

¹⁵ Baldwin and Simmons, *Trans. Faraday Soc.*, 1955, **51**, 680.

¹⁶ Baldwin, Corney and Simmons, *5th Int. Combustion Symp.* (Pittsburgh, 1954).

¹⁷ Lewis and von Elbe, *J. Chem. Physics*, 1942, **10**, 366.

¹⁸ Lewis and von Elbe, *Flame, Combustion and Explosion Processes in Gases* (Academic Press, New York, 1951).

¹⁹ Singer and Williams, *Ann. Reports*, 1948.

²⁰ Kondratiev and Kondratieva, *Acta Physicochim.*, 1946, **21**, 1.

²¹ Avramenko and Lorentzo, *Zhur. Fiz. Chim.*, 1950, **24**, 207.

²² Hartek and Kopsch, *Z. physik. Chem. B*, 1931, **12**, 327.

²³ Sanders, Shawlav, Dousmanis and Townes, *J. Chem. Physics*, 1954, **22**, 245.

²⁴ Linnett and Marsden, *Proc. Roy. Soc. A*, 1956, **234**, 504.

²⁵ Melville, *Trans. Faraday Soc.*, 1932, **28**, 308.

- ²⁶ Stefan, *Wiener Sitzungsberichte*, 1871, **63**, 63 ; 1872, **65**, 323.
²⁷ Maxwell, *Coll. Sci. Papers*, I, p. 393 ; II, p. 57, 345.
²⁸ Kennard, *Kinetic Theory of Gases* (McGraw Hill, 1938).
²⁹ Bonhoeffer and Harteck, *Grundlagen der Photochemie* (Steinkopff, Leipzig, 1937).
³⁰ Semenoff, *Acta Physicochim.*, 1942, **20**, 290.
³¹ Bertie and LeRoy, *Faraday Soc. Discussions*, 1953, **14**, 50.
³² Davidson, *Faraday Soc. Discussion*, 1954, **17**, 96.
³³ Baldwin and Walsh, *Faraday Soc. Discussions*, 1954, **17**, 96.
³⁴ Steacie, *Atomic and Free Radical Reactions* (Reinhold, New York, 1954).
³⁵ Lewis and Heiple, *J. Chem. Physics*, 1941, **9**, 584.
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