The Reaction Between Hydrogen and Oxygen: The Upper Explosion Limit and the Reaction in Its Vicinity

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The Reaction Between Hydrogen and Oxygen: The Upper Explosion Limit and the Reaction in Its Vicinity[1]

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We have found that water vapor effects a marked lowering of the upper explosion limit of hydrogen and oxygen. This is illustrated by the following typical results for a 2 : 1 mixture at 530°C, H_2O being admitted to the reaction vessel from a reservoir.

Percent H_2O	0	3.35	6.37	11.03
Upper limit, mm Hg	85.6	54.9	41.8	29.4

Nine determinations with water percentages ranging from 3 to 11 gave an average value of k_{6H_2O}/k_{6H_2} equal to 14.3, with a maximum error of 0.7. These results demonstrate that the water effect is no different in kind than the influence of other gases as described by the explosion condition

$$2k_2 = k_{6H_2}(H_2) + k_{6O_2}(O_2) + k_{6X}(X),$$

where X is water or any other inert gas. This equation corresponds to the reaction scheme

1. $OH + H_2 = H_2O + H$
2. $H + O_2 = OH + O$
3. $O + H_2 = OH + H$
6. $H + O_2 + (H_2, O_2, X) = HO_2 + (H_2, O_2, X)$.

The equation numbers follow those given elsewhere.[2]

The ratio k_{6O_2}/k_{6H_2} was determined at 530°C as 0.35 ±0.01 by observing the upper limit for mixtures of hydrogen and oxygen containing 20, 33.3, 50, and 66.7 percent hydrogen. The value showed no dependence on mixture composition. Similarly, k_{6X}/k_{6H_2} for other gases were found to be independent of the percentage present; for He, A, N_2 and CO_2 they are 0.36, 0.20, 0.43 and 1.47, respectively. The values for O_2, He, A and N_2 agree well with former determinations.[3]

On slowly approaching the upper limit from the high pressure side one may observe, very close to the limit, short bursts of reaction that die out rapidly, as is illustrated in Table I for a mixture containing 20 percent H_2 at 530°C.

TABLE I. *Initial pressure = 137.7 mm (upper explosion limit slightly below this).*

Time, sec.	0		15		23		30		37		100
$-dO_2/dt$, mm/min.		0.93		0.80		0.40		0.40		0.05	

The water thus formed pushes the limit toward lower pressures. That the water alone is responsible for this shift was shown by the precise agreement between the observed shift after allowing a known amount of water to be formed by reaction, and that calculated from the efficiency of water of 14.3.

A typical curve of the change of reaction rate with pressure above the upper explosion limit is shown in Fig. 1.

The Pyrex spherical reaction vessel, 7.2 cm in diameter, was heavily coated with KCl. The rates proved to be very well reproducible over a period of many weeks. They pass through a minimum, as expected. On the left side of the minimum the reaction inhibits itself (see above), and only initial rates are given.

We have also carried out upper-limit determinations in the same vessel from 400°C to 570°C. The values are considerably higher than those found by other investigators.[4] This and the occasional poor reproducibility found by these investigators may be explained by the water-vapor effect.

The foregoing observations furnish an explanation of most of the questions raised by Oldenberg and Sommers.[5]
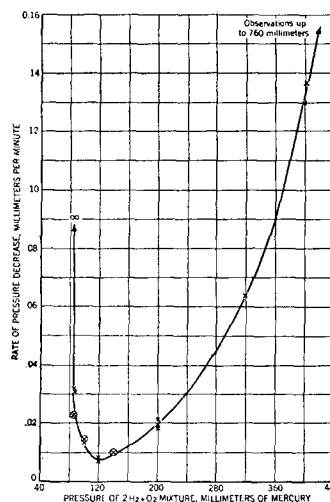

FIG. 1. Reaction rate of mixtures of $2H_2 + O_2$ at 530°C in spherical KCl-coated Pyrex vessel, 7.2 cm in diameter. ⊗ indicates duplicated observations.

The latter, working at 568°C, were unable to observe a minimum rate on approaching the upper limit. However, at this temperature the rates near the minimum are some 100 times greater than at 530°C, thus tending to obscure the branch of the curve to the left of the minimum by self-inhibition. Self-heating of the mixture, even of the order of 1°, should also contribute to this because the coefficient k_2 increases sharply with temperature; therefore, the transition between slow and explosive reaction becomes very abrupt. Oldenberg and Sommers' observation that the limit shifted from about 180 mm to about 120 mm after 4 percent of the mixture reacted is in striking agreement with the value of 14.3 for the water-vapor efficiency, the calculated shift being identical. It is also evident that the increase of the upper limit on coating the vessel with KCl, which these authors report, is caused by the decreased rate of water formation. The same limit can be found in both vessels by operating sufficiently fast.

We are making a detailed study of the kinetics of the hydrogen-oxygen reaction and shall publish further details

later, including a discussion of the remaining points raised by Oldenberg and Sommers.

[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior, and the Director, Coal Research Laboratory, Carnegie Institute of Technology.
[2] Lewis and von Elbe, *Combustion, Flames and Explosions of Gases* (Cambridge Univ. Press, 1938), p. 33.
[3] G. H. Grant and C. N. Hinshelwood, Proc. Roy. Soc. (London) A141, 29 (1933); A. A. Frost and H. N. Alyea, J. Am. Chem. Soc. 55, 3227 (1933).
[4] H. W. Thompson and C. N. Hinshelwood, Proc. Roy. Soc. (London) A122, 610 (1929); A. A. Frost and H. N. Alyea, reference 3; G. H. Grant and C. N. Hinshelwood, *ibid.*
[5] O. Oldenberg and H. S. Sommers, J. Chem. Phys. 8, 468 (1940).

Coriolis Perturbations and Molecular Dimensions in Germane GeH$_4$

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In a recent paper Murphy[1] has calculated the structure of the ν_4 fundamental in SiH$_4$ and in GeH$_4$ by evaluating the matrix elements of the coriolis perturbations between ν_4 and the doubly degenerate ν_2. It was found that these perturbations satisfactorily explain the observed complexities in these bands and in particular the unsymmetrical shapes of the Q branches. While the agreement between the observed and the calculated structure is good in the case of SiH$_4$, it is less so in the case of GeH$_4$. The purpose of this note is to suggest that the poorer agreement is probably due to the use of a vlaue for the moment of inertia of GeH$_4$ which is highly questionable.

Steward and Nielsen estimated I at 7.0×10^{-40} g cm^2 for GeH$_4$ from the spacings $\Delta\nu_3 = 5.56$, $\Delta\nu_4 \sim 6$ cm^{-1} according to the theory of Teller and of Johnston and Dennison. This value of I yields the value 1.27A for the Ge-H distance which has been pointed out by the writer to be unreasonable on comparison with the Si-H distance in SiH$_4$.[2] On account of the complexities in the structure of ν_4 due to the perturbation by ν_2, the $\Delta\nu_4$ has no strict meaning and must hence not be used in determining I. On the other hand, the assumption of pure valence and deformation forces in such molecules as CH$_4$, SiH$_4$, GeH$_4$ is probably a good approximation. On this assumption and from the observed value of $\Delta\nu_3$ in the ν_3 band which is not perturbed by ν_2, we obtain the following dimensions (Table I). These values of I are also only approximate since the internal angular momenta ξ's obtained on the assumption of pure valence force system are approximate, as can be seen in the case of CH$_4$ in which the C$-$H distance is known to be 1.09A. Their relative values are, however, more reasonable than those obtained by employing $\Delta\nu_3$ and $\Delta\nu_4$ since one would expect the Ge-H distance to be greater than Si-H. It is hoped that the use of $I \simeq 9.8 \times 10^{-40}$ g cm

TABLE I.

	$\Delta\nu_3$	ξ_3	ξ_4	$I = \dfrac{(1-\xi_3)h}{4\pi^2\Delta\nu_3}$	X$-$H	FROM $\Delta\nu_3$ AND $\Delta\nu_4$ I	X$-$H
CH$_4$	9.77	0.100	0.400	5.09×10^{-40}	1.07A	5.47×10^{-40}	1.11A
SiH$_4$	5.65	0.046	0.454	9.34 "	1.45	8.9 "	1.41
GeH$_4$	5.56	0.018	0.482	9.77 "	1.49	7.0 "	1.27

for GeH$_4$ in the perturbation calculations will improve the agreement between the calculated and the observed structure of ν_4.

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[2] T.-Y. Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (National University of Peking), pp. 230–231.

Conductivity of Calcium Salts

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It is of interest to the medical world to prevent convulsive effects that usually follow the administration of certain anesthetics. Drs. R. Beutner and G. P. Miley,[1, 2] Department of Pharmacology, Hahnemann Medical College, observed that the simultaneous injection of certain calcium salts with these anesthetics inhibited convulsions. Dr. Beutner[3] suggested that the action of the salt could be correlated with its calcium ion content, that a measurement of the salt's electrical conductivity would be of interest to the formulation of a theory of the salt's physiological action.

Since there were found in the literature almost no data on the electrical conductivities of the salts used in the animal experiments,[4] we measured them, using the standard Kohlrausch bridge method with 60-cycle current and a conductivity cell with Pt electrodes, at 18°C, and the following results (Table I) were obtained:

TABLE I.

SALT	0.1 N	σ IN MHO/CM 0.01 N	0.001 N
Ca Gluconate	2.52×10^{-3}	4.97×10^{-4}	6.92×10^{-5}
Ca Benzoate	2.68	7.25	8.46
Ca Lactate	3.79	6.40	9.50
Ca Levulinate	4.75	6.55	8.13
Ca Salicylate	5.35	7.50	9.49
Ca Chloride	8.62	10.1	12.5
Ca Bromide	9.10	10.7	10.1

Calcium gluconate held special interest to the pharmacologist, so further detailed measurements were made on it (Table II).

TABLE II.

	CONCENTRATION	AVERAGE CONDUCTIVITY
18°C	0.1 N	2.52×10^{-3} mho/cm
	0.05 N	1.62×10^{-3} "
	0.01 N	4.97×10^{-4} "
	0.005 N	2.75×10^{-4} "
	0.001 N	6.92×10^{-5} "
25°C	0.1 N	3.24×10^{-3} mho/cm
	0.01 N	6.50×10^{-4} "

Deviation for these readings was within ±3 percent.

These measurements were made in the Pharmacology Department of the Hahnemann Medical College.

[1] R. Beutner and G. P. Miley, Proc. Soc. Exp. Biol. Med. 38, 279 (1938).
[2] R. Beutner and G. P. Miley, Proc. Soc. Exp. Biol. Med. 42, 547 (1939).
[3] R. Beutner, Am. J. Physiol. 129, 489 (1940).
[4] Curr. Researches in Anes. and Analgesia 19, 132 (1940).