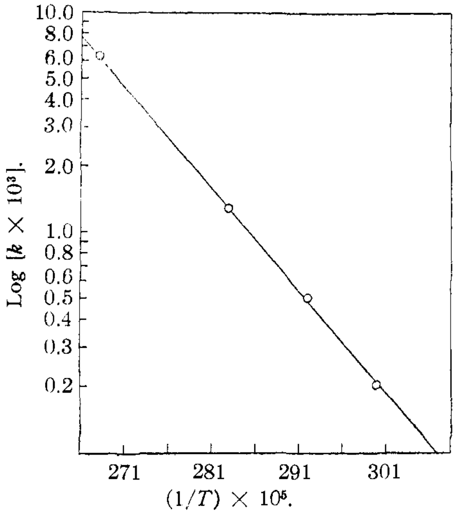

Fig. 2.

activation energy the parameter A of the modified Arrhenius equation

$$\log \frac{k}{\sqrt{T}} = A - \frac{E}{4.57T}$$

may be evaluated and in turn the effective collision diameter can be calculated from

$$\log \frac{k}{\sqrt{T}} = \log [6.06 \times 10^{20} \sigma^2 (8\pi R/M)^{1/2}] - \frac{E}{4.57T}$$

The value found for A is 8.8 and σ = 1.3 Å. The value found for the activation energy and the effective collision diameter are in accord with those found by Elliott and Sugden[12] in their studies of bromide exchanges in a series of alkyl bromides.

Acknowledgment.—The apparatus used in this research was built with the aid of a grant from the Research Corporation.

Summary

The exchange of bromide ions with α-bromopropionic acid was studied in aqueous solution and the activation energy was determined. The reaction obeyed the Arrhenius equation to within experimental error and the value of the effective collision diameter was found to be about what would be expected from simple collision theory. The values of the activation energy and collision diameter are in accord with other similar work.

[12] G. A. Elliott and S. Sugden, *J. Chem. Soc.*, 1836 (1939).

BALTIMORE, MARYLAND RECEIVED MAY 19, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Rates of Reaction of Excited Mercury with Oxygen, Hydrogen Sulfide and Nitrous Oxide, and their Relation to Effective Collision Diameters

BY JAMES E. CLINE AND GEORGE S. FORBES

Introduction.—This investigation was undertaken to correlate the quantitative dependence of reaction rate on pressure with effective collision diameters in reactions involving mercury excited by resonance radiation. Effective collision diameters have been estimated through studies of the quenching of mercury fluorescence by various gases. Of numerous papers a few may be cited.[1–4] Zemansky[3,4] corrected his results for reabsorption of fluorescence radiation. Frank[5] concluded that reaction rate is proportional to intensity of resonance radiation (λ = 2537 Å.) and that radiation of wave length less than 2000 Å. is without influence upon the reaction. His further conclusions are discussed below. Leipunski and Sagulin[6] had shown that this resonance radiation is necessary for the reaction, but Noyes[7] had stated that participation of shorter wave lengths also was required for explanation of his results.

With new methods of correction for experimental complications, we have reinvestigated the reaction of oxygen with excited mercury, and have studied hydrogen sulfide and nitrous oxide as well. Our theoretical interpretation takes into consideration the mean lifetime of excited mercury, the quenching efficiency of foreign gas and the reabsorption of fluorescence radiation by mercury. In this way the effects of pressure, temperature and geometry of reaction vessel can be explained.

The well-known Stern–Volmer equation for quenching of fluorescence radiation can be obtained starting from

$$0 = \frac{d[\mathrm{Hg}^*]}{dt} = kI - k_2[\mathrm{Hg}^*]p - k_3[\mathrm{Hg}^*] \quad (1)$$

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(1) Stern and Volmer, *Physik. Z.*, **20**, 183 (1919).

(2) Stuart, *Z. Physik*, **32**, 262 (1925).

(3) Zemansky, *Phys. Rev.*, **31**, 812 (1928).

(4) Zemansky, *ibid.*, **36**, 919 (1930).

(5) Frank, *Acta Physicochim.* (U. S. R. R.), **1**, 833 (1934).

(6) Leipunski and Sagulin, *Z. physik. Chem.*, **B1**, 362 (1928).

(7) Noyes, THIS JOURNAL, **49**, 3100 (1927).

Here I is the light flux absorbed by mercury in a steady state, p the pressure of the foreign gas, $[Hg^*]$ the number of excited mercury atoms per cc., k_2 the rate of effective collisions per second per mercury atom with molecules of foreign gas at 1 mm. pressure, and $k_3 = 1/\tau$ where τ (tau) is the mean lifetime of an excited mercury atom. If $S/S_0 = J$, where S and S_0 represent observed fluorescence radiation with and without foreign gas under conditions otherwise identical, the Stern–Volmer equation follows

$$J = 1/[1 + k_2p/k_3] \qquad (2)$$

Stuart[2] wrote

$$k_2 = 2\sigma^2 n \sqrt{2\pi RT(m_1 + m)/m_1 m} \qquad (3)$$

and introduced k_2 as calculated from his quenching experiments, whereupon σ the effective collision diameter was obtained.

Foote[8] improved Stuart's treatment by taking account of reabsorption of fluorescence radiation so that

$$0 = \frac{d[Hg^*]}{dt} = k_1I - k_2[Hg^*]p - kf[Hg^*] \qquad (4)$$

where f, the fraction of fluorescence radiation which escapes, is a function of mercury pressure and the geometry of the vessel. Thus evaluated

$$J = 1/[1 + k_2p/(k_3f)] \qquad (5)$$

In the Stern–Volmer equation, employed also by Stuart, the tacit assumption is made that $f = 1$.

Zemansky[4] devised a method for measuring the fluorescence radiation escaping in the direction of the axis of his vessel. He calculated J as a function of k_2p/k_3 through a complicated integration based on Milne's theory.[9] We found that the plot of this function strongly resembles a plot of equation (5) where f is set equal to 0.12.

The object of our investigation was to account for the dependence of our reaction rates upon p, and for the effects of changing temperature. The first step was to transform equation (4) as follows

$$[Hg^*] = k_1I/(k_2p + k_3f) \qquad (6)$$

Under the assumption, which will presently appear reasonable, that the secondary reactions following each effective collision are unchanged over the moderate pressure range investigated

$$-\frac{dp}{dt} = R = k_4k_2p[Hg^*] \qquad (7)$$

in which k_4 connects collision numbers with measured rates. From (6) and (7)

$$R = (k_1k_2k_4Ip/k_3)/(k_2p/k_3 + f) \qquad (8)$$

Writing $k_1k_2k_4I/k_3f = A$ and $k_2/k_3f = B$

$$R = Ap/(1 + Bp) \qquad (9)$$

As pressure increases, R approaches A/B as a maximum. When R is one-half the maximum rate, then $R_{1/2} = A/2B$. The "half pressure" $p_{1/2}$ corresponding to $R_{1/2}$ results from (9)

$$p_{1/2} = 1/B \qquad (10)$$

Apparatus.—The quartz reaction cell C (Fig. 1) had been designed to permit maximum utilization of the energy emitted by the resonance lamp L (Braun Corporation "Fluorolight"), the luminous column of which extended within 2 cm. of the bottom of the inner quartz tube. This tube contained either distilled water, or a light-filter solution, as occasion required. The difference in radius of the two concentric tubes was about 1 cm., and the corresponding annular space contained the reacting gas, kept saturated with mercury vapor from a cubic centimeter of liquid mercury on the bottom, which could also be condensed upon the inner surface of the outer wall. The reaction cell was connected through a quartz–Pyrex seal (not shown) to the mercury valve M, which went into action when mercury was admitted from R, and the left limb was evacuated. The stopcocks V and A were connected to a vacuum and to the atmosphere, respectively, to control the pressure in R. The cell was immersed in a water thermostat T with a stirrer and a thermoregulator (not shown).

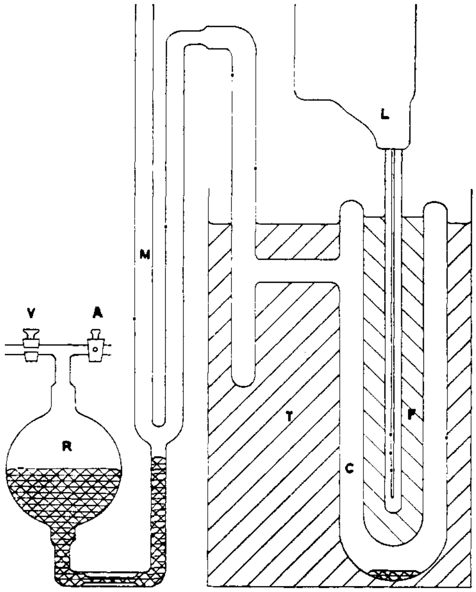

Fig. 1.—Diagram of apparatus.

Materials.—Mercury was freed from air and water by several distillations in a high vacuum.

Oxygen was prepared by heating mercuric oxide in a side-tube (not shown) communicating with the evacuated system. The oxide had previously been heated in a vacuum to incipient decomposition to eliminate water and gases more readily liberated than oxygen.

The hydrogen sulfide was a sample of highly purified

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(8) Foote, *Phys. Rev.*, **30**, 288 (1927).

(9) Milne, *J. London Math. Soc.*, **1**, Part I (1926).

material previously described.[10] It was stored over mercury, the surface of which remained bright at all times.

Nitrous oxide was taken from a small cylinder (S. S. White), passed over sodium hydroxide, frozen out with liquid air, and the residual gases pumped off in a high vacuum. The vessel containing the nitrous oxide was then surrounded with solid carbon dioxide, and the first portion of nitrous oxide was allowed to evaporate into a suitable storage vessel.

Measurement of Reaction Rates.—The rate of photosensitized reaction between mercury vapor and oxygen was determined from successive measurements of the total pressure of the system on a McLeod gage. The highest pressure which could be measured thus was 1 mm. Pressure differences could be determined within 4×10^{-4} mm. at 1 mm., and within 10^{-5} mm. at 0.002 mm. total pressure. Reaction rates of hydrogen sulfide and nitrous oxide were followed by measuring the pressure of gas not condensed after an hour's immersion in liquid air. In the experiments on nitrous oxide the total pressure was unchanged by irradiation. Therefore it was inferred that the uncondensable reaction product measured on the gage was nitrogen, rather than nitrogen plus half a molecule of nitric oxide, a mixture which would have been formed with increase in volume.

During irradiation, mercury vapor was consumed through deposition of a film of mercuric oxide or mercuric sulfide upon the walls of the vessel. Through evaporation, and diffusion of mercury vapor, a steady state lower than saturation pressure was attained. To correlate results in any series of experiments at a fixed temperature, light absorption at the highest reaction rate must approximate that corresponding to saturated mercury vapor. Realization of this condition should be promoted either by increased temperature or by lowered light intensity. Even when the radiation flux of our lamp was somewhat weakened by solid deposits, the reaction rate at 35° was roughly three times that at 25° at a comparable oxygen pressure. Evidently the steady state attained at 25°, at least, did not approximate complete light absorption. Therefore a cylindrical screen of lead foil perforated with numerous pinholes transmitting less than one per cent. of the light was employed to cut down the light intensity. Alternations of temperature between 25 and 45° were now practically without effect upon reaction rate of oxygen, as shown in Table I.

TABLE I

EFFECT OF TEMPERATURE AT REDUCED LIGHT INTENSITY

Mean p_{O_2}	t, °C.	Rate, mm./min.
0.308	35	0.000074
.287	25	.000074
.280	45	.000088
.245	25	.000075
.230	45	.000061

Deposition of solid mercury compounds was, of course, most pronounced upon the surface through which light entered, so that reaction rates were progressively reduced. Evans[11] in studying the photosensitized hydrogen–oxygen reaction, recognized the consequences of such accentuations, but Frank[5] apparently did not realize their importance. In a previous investigation[12] and also in some of the present experiments upon hydrogen sulfide, the difficulty was met by use of a large quartz cylinder rotated in such a manner that the solid product was evenly distributed as a film of negligible absorptive power over the entire internal surface. The vessel shown in Fig. 1 was ordinarily used, so that observed rates, R', had to be corrected for absorption of radiation by deposits on the walls. We expressed the thickness of the layer in terms of total reaction up to any given time, and also assumed that $\log I_0/I$ was proportional to this thickness. If now R/R' is the ratio of corrected to uncorrected rate under given conditions

$$\log \frac{R}{R'} = \log \frac{I_0}{I} = k\Delta p \qquad (11)$$

or

$$k = \frac{1}{\Delta p} \log \frac{R}{R'} \qquad (12)$$

TABLE II

CORRECTION FOR ABSORPTION BY DEPOSITED MERCURIC OXIDE

Δt	p	R'	Δp	$\frac{1}{\Delta p} \log \frac{0.0178}{R'}$	R	$\frac{1}{\Delta p} \log \frac{R}{R'}$
0	0.967					
		0.0178	0.0	..	0.0178	..
5	.878					
		.0104	.071	3.29	.0177	3.26
10	.826					
		.0104	.123	1.90	.0177	1.88
15	.774					
		.0058	.166	2.93	.0176	2.91
21	.739					
21	.730					
		.0041	.204	3.12	.0176	3.10
31	.689					
		.0032	.242	3.08	.0176	3.06
42	.654					
		.00223	.284	3.17	.0175	3.15
64	.605					
94	.551	.0018	.336	2.96	.0174	2.94
128	.504	.00138	.386	2.88	.0173	2.85
158	.469	.00117	.427	2.77	.0171	2.73
218	.408	.00102	.475	2.62	.0170	2.58
278	.361	.00078	.529	2.57	.0168	2.52
			Average	2.84		2.82

Table II gives particulars for oxygen. As a first approximation, assume that R as defined in equation (7) is independent of pressure, and is 0.0178 corresponding to R' at $\Delta p = 0$. Then successive values of k result from measurements of R' and Δp. From experiments later described, R was calculated as a function of pressure and inserted in column 6. Then k was recalculated from equation (9) and inserted in column 7. It is seen that the small correction for R in this pressure

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[10] Avery and Forbes, THIS JOURNAL, **60**, 1005 (1938).

[11] Evans, *J. Chem. Phys.*, **2**, 726 (1934).

[12] Forbes, Cline and Bradshaw, THIS JOURNAL, **60**, 1431 (1938).

range has not greatly affected the value of *k*. Average values for *k* are as follows

$$k_{O_2} = -2.82\ \Delta p_{O_2},\ k_{H_2S} = 5.7\ \Delta p_{H_2},\ k_{N_2O} = 1.18\ \Delta p_{N_2}$$

Correction for Reverse Reaction.—Scheele,[13] in 1777, was the first to note the photolysis of mercury oxide, which occurs even in strong sunlight. We exposed to the radiation of the unshielded lamp a deposit absorbing 90% of the light, and present in a vacuum of 7×10^{-5} mm. The initial rate of pressure increase was 2.2×10^{-4} mm./minute and the final steady state was reached at 0.0027 mm. The evolved gas was pumped out and the deposit again irradiated with the same results. We assumed that the rate of this reverse reaction was proportional to light flux absorbed by the deposit. The corresponding correction was found to be necessary in only a few experiments, at 45°, with the unshielded lamp and deposits absorbing 80 to 90% of incident light.

Frank's Results for Oxygen.—Frank[5] wrote

$$dp/dt = c\alpha p/(1 + \alpha p) \qquad (13)$$

identical in form with (9). He integrated it between t_1 and t and then selected his constants to fit one, only, of his two experimental curves. In Fig. 2 we have plotted his rates against pressures (Frank plotted pressures against time). The experiment represented by circles covered only a small range of pressures, so that the deposit of mercuric oxide may not have been serious. He selected $\alpha = 4.8$ as the "best" value for this curve, which is not far from our own result. However, his pressure range was insufficient to confirm his value of α, as is evident when one considers also the curve corresponding to $\alpha = 2.4$ which we have drawn in for comparison. The points in squares he obtained starting with a relatively high pressure, in a reacting volume half as great, but ignored them in his calculation of α. These points indicate to us a rapidly increasing extinction of radiation by mercuric oxide rather than a half pressure greatly exceeding that in the left-hand curve.

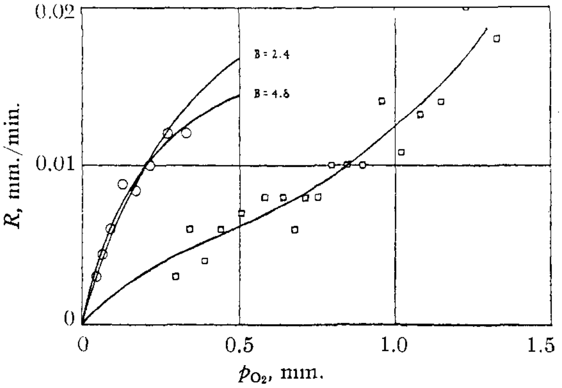

Fig. 2.—Rate of reaction and pressure of oxygen from data of Frank.

Results on Oxygen.—We found by the use of light filters that radiation of wave length less than 2537 Å. is not necessary for the photosensitized mercury–oxygen reaction. This is in agreement with Frank,[5] but contrary to the conclusions of Noyes.[7] Figure 3 shows *R*, the fully corrected reaction rates at 45° in mm. per minute, plotted against total pressure in the reaction vessel.

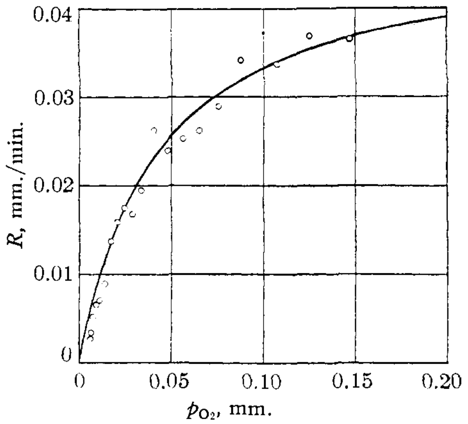

Fig. 3.—Rate of reaction and pressure of oxygen at 45°.

These corrected rates correspond to the full intensity of the lamp. The curve is drawn according to equation (9), obtaining the "best" values of the two constants by trial.

$$R = \frac{Ap}{1 + Bp} = \frac{1.16\ P}{1 + 25\ P}\ \text{mm./minute}$$

Additional experiments at 45° were undertaken to prove the validity of equation (9) at higher pressures. At 0.727 mm. and 0.166 mm. the rates were 0.00165 and 0.00144 mm./minute, respectively, when corrected back not to full intensity of the lamp but to a particular deposit of mercuric oxide. Upon division, the constant *A*, which depends on light intensity, disappears.

$$\frac{R_1}{R_2} = \frac{1 + Bp_2}{1 + Bp_1}\frac{p_1}{p_2} \qquad (14)$$

The experimental ratio of reaction rates is 1.15. Substituting the value $B = 25$ in equation (10) the ratio of reaction rates is predicted to be 1.18, which is a satisfactory agreement.

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[13] See Plotnikow, "Lehrbuch der Photochemie," Walter de Gruyter, Berlin and Leipzig, 1920, p. 459.

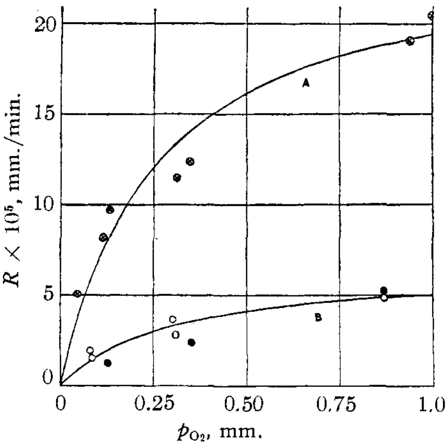

Fig. 4.—Rate of reaction and pressure of oxygen at 25 and 0°.

Figure 4 shows R at 25° (curve A) and R at 0° (curve B). Because of the slower evaporation and diffusion of mercury at these temperatures, the lamp was shielded by the perforated screen of lead foil described above which transmitted somewhat less than one per cent. of the incident light. As each open circle (curve B) represents the difference between two averaged pressures, each of which was read three times, these points are given greater weight than the black circles where this additional precaution was not taken. Otherwise following the procedure described for the results at 45°

$$R = \frac{0.00097\,p}{1 + 4.0\,p} \text{ at } 25°$$

and

$$R = \frac{0.00022\,p}{1 + 3.3\,p} \text{ at } 0° \text{ in mm./minute}$$

The half pressures, $p_{1/2}$, equal to $1/B$, at 45, 25 and 0°, are 0.04, 0.25 and 0.3 mm., respectively. From quenching data Stuart[2] obtained a value of 0.35 mm. and Zemansky[4] 0.15 mm. Referring to (8) it appears that

$$1/B = k_3 f/k_2 \tag{15}$$

in which k_3 is independent of T, and k_2 from equation (3) depends upon $1/\sqrt{T}$. Then $f \sim 1/B\sqrt{T}$, or $f_{45°}:f_{25°}:f_{0°} = 1:6:8$. The fraction of fluorescence radiation which escapes increases with falling temperature as it should, but the values of B are not accurate enough to give clear evidence of the nature of the function.

The values of σ^2/f can now be calculated from (3) and (15) by introducing B as determined for each temperature, and by writing[14] $k_3 = 1/\tau = 9.26 \times 10^{-6}$ sec. At 45, 25 and 0°, $10^{16}\sigma^2/f$ becomes 480, 76 and 76 cm.², respectively. From viscosity measurements $\sigma = r_{O_2} + r_{Hg} = (1.75 + 1.51)\ 10^{-8}$ cm., where mercury is in the ground state. Neglecting the difference $r_{Hg*} - r_{Hg}$, $\sigma^2 = 10.6 \times 10^{-16}$. Zemansky[3] corrected Stuart's results for reabsorption of fluorescence radiation and obtained $\sigma^2 = 20 \times 10^{-16}$. By correction of his own measurements he obtained $\sigma^2 = 13.6 \times 10^{-16}$. If we accept this outcome, at 0°, for oxygen and excited mercury, $f = 1/4$ approximately.

Results on Hydrogen Sulfide.—To establish with greater certainty the relation of light intensity to the constants k_2 and k_3, experiments were undertaken at 23° in a large rotating cylindrical cell previously described.[12] A sodium nitrate filter 0.005 M and 10 mm. thick removed radiation of wave length less than 2400 Å. to avoid, so far as possible, an unsensitized photolysis. As the effective surface was very nearly three times that of the annular cell, $k'_{H_2S} = k_{H_2S}/3 = 1.9\ \Delta p_{H_2}$. The larger surface, cleaned by ignition at the start, and again before each change in light intensity, required relatively small corrections. Curves A, B and C in Fig. 5 were plotted as usual with the unshielded lamp 6, 15 and 34 cm. from the outer wall of the cylinder.

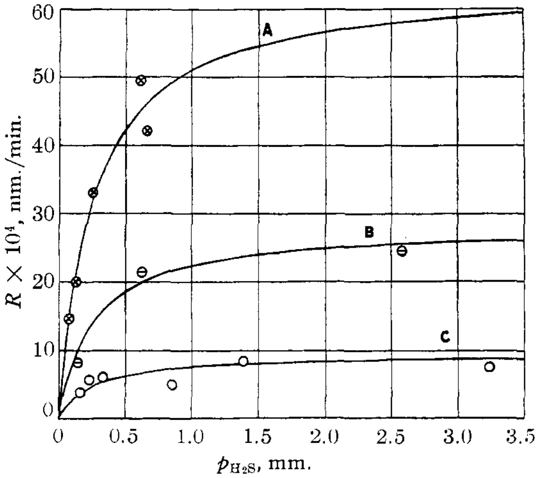

Fig. 5.—Rate of reaction and pressure of hydrogen sulfide at 22° in rotating cell.

The "best" curves are

$$R_A = 0.025\,p/(1 + 4p)$$
$$R_B = 0.011\,p/(1 + 4p)$$

and

$$R_C = 0.0037\,p/(1 + 4p)$$

Clearly, the constant A depends on light intensity, but B does not. The values of $p_{1/2}$, the half pres-

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[14] Garrett, *Phys. Rev.*, **40**, 779 (1932).

sure at 23°, are 0.25 mm. in each case corresponding to $\sigma^2/f = 77 \times 10^{-16}$ cm.^{2}.

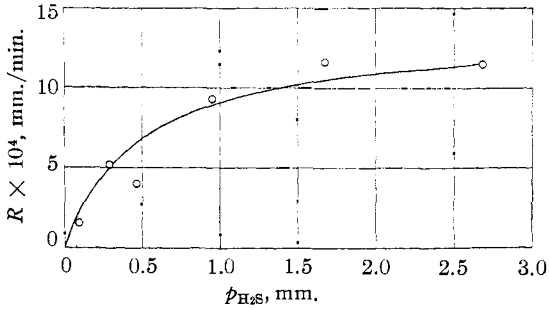

Fig. 6.—Rate of reaction and pressure of hydrogen sulfide at 0°.

Results for the annular cell at 0° are plotted in Fig. 6. After each measurement of pressure the mercuric sulfide was removed by lowering a hot copper bar inside the highly evacuated cell. Thus the correction for the deposit was not cumulative. $R = 0.0027\ p/(1 + 2.0\ p)$, and $p_{1/2} = 0.5$ mm. corresponding to $\sigma^2/f = 37 \times 10^{-16}$ cm.^{2}. The fact that R becomes practically independent of p at pressures considerably greater than $p_{1/2}$ indicates that the secondary reactions following each effective collision are unchanged over the pressure range investigated. Thus the corresponding assumption made in deriving equation (7) appears justified.

Results on Nitrous Oxide.—The annular cell at 0°, only, was used. Attempts were made to remove mercuric oxide by pumping the cell flat and introducing boiling water after each pressure reading. But it was found that the observed rate following such treatment, though readily reproducible, was only about half that in a vessel just cleaned with nitric acid and ignited in a high vacuum. It was evident that a thin layer of deposit next to the glass was much less volatile than superimposed layers. The circles (Fig. 7) represent rates corrected to the light flux transmitted by this relatively involatile layer. $R = 0.0028\ p/(1 + 3.1p)$, and $p_{1/2} = 0.32$ mm., corresponding to $\sigma^2/f = 64 \times 10^{-16}$ cm.^{2}.

Assuming that f at 0° is independent of the nature of the foreign gas

	O_2	N_2O	H_2S
$\sigma^2 \times 10^{16}$ cm.^{2} (viscosity)	10.6	13.5	12.6
$(\sigma^2/f) \times 10^{16}$ cm.^{2} (reaction rate)	60	64	37

where σ is the sum of two collision radii. Quenching data for nitrous oxide and hydrogen sulfide were not found in the literature, but from our data it appears that within the limit of error the quenching efficiencies of oxygen, nitrous oxide and hydrogen sulfide are in the ratio 1.0 to 0.8 to 0.5.

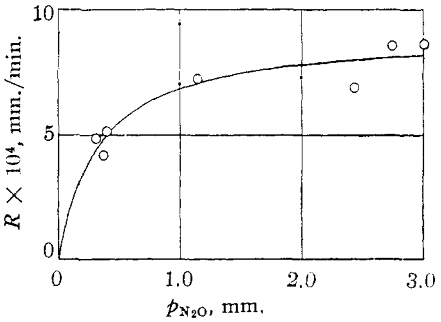

Fig. 7.—Rate of reaction and pressure of nitrous oxide at 0°.

Summary

Reaction rates of excited mercury with oxygen, hydrogen sulfide and nitrous oxides were obtained and corrected for light absorption by solid mercury compounds, also, when necessary, for photolysis of mercuric oxide.

Light intensity was reduced to a point such that depletion of mercury vapor by chemical reaction was very small, and light absorption corresponded, within experimental error, to absorption by saturated mercury vapor.

The half pressures, corresponding to half the maximum reaction rate at a given temperature, were evaluated for each gas at 0°, and for oxygen at 25 and 45° as well. The half pressure of oxygen thus obtained is intermediate between the two best values obtained by previous investigators from quenching experiments at corresponding temperatures. Radiation of wave length less than 2537 Å. is not necessary for the photosensitized mercury–oxygen reaction.

The ratio σ^2/f was calculated for each of the three gases. Here σ is the sum of collision radii with mercury and f the fraction of fluorescence radiation escaping reabsorption under our experimental conditions.

Comparing σ^2/f thus obtained with σ^2 from viscosity measurements, we predict that the quenching efficiencies of oxygen, nitrous oxide and hydrogen sulfide upon resonance radiation are in the ratio 1.0 to 0.8 to 0.5.

CAMBRIDGE, MASSACHUSETTS RECEIVED MAY 22, 1941