is about 8%. At least a part of this difference may be due to experimental error.

8. Further work is contemplated to obtain better experimental results.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

QUENCHING OF THE FLUORESCENCE OF NITROGEN DIOXIDE

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Of late the photochemical decomposition of nitrogen dioxide into nitric oxide and oxygen has been the object of several investigations.[2] That the absorption spectrum of nitrogen dioxide in the visible and near ultraviolet regions of the spectrum is discrete is well known.[3] Recently, Mecke[4] and Henri[5] have noted that predissociation occurs in this gas, the bands first becoming diffuse between 3800 and 3700 Å. The light absorption process in this region corresponds to the beginning of formation of an excited molecule followed by immediate dissociation into nitric oxide and oxygen. Fluorescence is to be expected in nitrogen dioxide at sufficiently low pressures when one illuminates with wave lengths above the limit of predissociation. Indeed, due to the ineffectiveness of blue light, 4358 Å., in causing photodecomposition, Norrish was led to conclude that all of this light must be reradiated. Norrish[6] succeeded in obtaining the expected fluorescence which appears as a faint yellowish luminescence when nitrogen dioxide is illuminated with the 4358 and 4047 Å. lines of the mercury arc. The spectra emitted are identical under excitation by either λ4358 or 4047, consisting of two wide maxima at 6400 and 5900 Å., except that the intensity of the 5900 band is relatively more intense with the shorter wave length. With λ3660 there is only an extremely feeble fluorescence, also in this same region. The almost complete absence of fluorescence by this light is indeed in keeping with the idea that immediately after light absorption, dissociation of the excited molecule takes place.

The object of the present investigation is the study of the intensity of the fluorescence as a function of the pressure both of nitrogen dioxide itself and of added gases. Such measurements afford quantitative data concerning the efficiencies of deactivating collisions, quantities of considerable importance in chemical kinetics.

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[1] National Research Fellow in Chemistry.

[2] Norrish, *J. Chem. Soc.*, 761 (1927); Dickinson and Baxter, THIS JOURNAL, **50**, 774 (1928); Norrish, *J. Chem. Soc.*, 1158, 1604, 1611 (1929).

[3] Harris, *Proc. Nat. Acad. Sci.*, **14**, 690 (1928).

[4] Mecke, *Naturwissenschaften*, **17**, 996 (1929); *Z. physik. Chem.*, **7B**, 108 (1930).

[5] Henri, *Nature*, **125**, 202 (1930).

[6] Norrish, *J. Chem. Soc.*, 1611 (1929).

Experimental Arrangement

The fluorescence vessel was a pyrex tube, 4 cm. in diameter, with a fused-on plane end window and a side tube for applying liquid air. Connection was made through a stopcock to a reservoir of known volume (213.1 cc.) which led through a second cock to a liquid-air trap and a device for magnetically breaking small bulbs filled with nitrogen dioxide at a known pressure, and finally through another stopcock to a liquid-air trap and mercury diffusion pump. The method of introducing nitrogen dioxide was essentially that used previously.[7] The volume of the fluorescence vessel was 109.3 cc. Thus, once the fluorescence vessel had been filled with a known amount of nitrogen dioxide, the pressure could be reduced in definite steps by expansion into the evacuated reservoir. In this manner a complete set of runs could be made on a single sample of gas over the desired pressure range. Other gases (H_2, N_2, O_2, CO_2) were added from a bulb containing them through a stopcock buret. These gases were taken directly from tanks and purified by drying over phosphorus pentoxide.

The light source was a mercury arc run at atmospheric pressure. After the light had passed through suitable filters, it was collimated by lenses and diaphragms before entering the window of the fluorescence vessel. In order to observe the rather feeble fluorescence it was necessary to enclose the arc and completely darken the room.

The intensity of the fluorescence was determined by a method of visual photometry. A beam of light from a small filament passed through two Nicol prisms, one of which could be rotated, and struck a small piece of cardboard placed between the eye of the observer and the path of the irradiating light as outlined by the fluorescence. The point in the beam at which the comparison of intensities was made was 3 cm. from the window the light entered. A yellow filter cut out the small amount of scattered blue and violet light. With this simple photometer it was found possible to obtain quite reproducible matches; an average of at least five settings was taken as representing a fairly accurate measure of the intensity of the fluorescence.

Fluorescence in Pure Nitrogen Dioxide.—When nitrogen dioxide is illuminated with λ4358 or 4047 Å., the incident beam is clearly outlined when viewed at right angles. The fluorescent light appears nearly white or slightly yellowish. No fluorescence was observable when illumination was made with λ3660.

In Table I are given the experimental results on the relative intensities of the fluorescence in pure nitrogen dioxide for the pressures investigated. Illumination was made with the λ4358 and 4047 lines of the mercury arc, used together to secure sufficient intensity. In the first two columns are given the pressures of nitrogen dioxide and nitrogen tetroxide, in the third the observed intensity. The fourth column gives the fractional transmission of light through the 3-cm. layer of nitrogen dioxide up to the point of observation. This was calculated for each of the pressures from Beer's law, $I = I_0e^{-\alpha lp}$, with $\alpha = 0.0192$ per cm. per mm. pressure of nitrogen dioxide. The absorption coefficients of nitrogen dioxide for λ4358 and for λ4047 were obtained incidental to some photochemical experiments and are the same within a few per cent. With the aid of a spectral photometer, Beer's law was found to hold between 4.5 and 0.3 mm. pressure and should presum-

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[7] Dickinson and Baxter, This Journal, 50, 774 (1928).

ably hold down to the lowest pressures used here. For small absorption, Beer's law reduces to the form that the absorption is proportional to the pressure. Therefore, the observed intensities, divided by the transmission and by the pressure of nitrogen dioxide, give the relative intensities of the fluorescence for the same quantity of light absorbed.

TABLE I

INTENSITY OF FLUORESCENCE IN NITROGEN DIOXIDE

Illumination by 4358 and 4047 Å. lines of mercury arc

p_{NO_2}, mm.	$p_{N_2O_4}$, mm.	Observed intensity	Transmission	$I_{\text{corrected}}$	$I = \frac{I_{\text{corr.}}}{p_{NO_2}}$	$\frac{I_0}{50p_{NO_2} + 1}$
13.9	2.92	0.0625	0.449	0.139	0.0100	0.0119
5.71	0.49	.1260	.720	.175	.0307	.0289
2.13	.07	.1468	.884	.166	.0780	.0772
0.753	.009	.1600	.958	.167	.222	.215
.259	.001	.1600	.985	.162	.626	.595
.0883	..	.1282	.995	.129	1.44	1.53
.0299	..	.0974	.998	.0976	3.26	3.32
.0102	..	.0586	.999	.0586	5.75	5.50
.00345	..	.0208	1.000	.0208	6.03	7.07
.00117	..	.0102	1.000	.0102	8.72	7.85
			Run 2			
18.3	4.01	0.0499	0.349	0.143	0.0078	0.0064
7.57	0.68	.0790	.647	.122	.0161	.0156
2.84	.10	.1018	.849	.120	.0422	.0412
1.00	.01	.1023	.944	.108	.108	.116
.345	.001	.1190	.980	.122	.354	.323
.118	..	.1018	.993	.103	.873	.855
.0400	..	.0806	.998	.0808	2.02	1.97
.0136	..	.0466	.999	.0466	3.43	3.51
.00460	..	.0243	1.000	.0243	5.29	4.80
.00156	..	.0074	1.000	.0074	4.74	5.48

The excited molecule of nitrogen dioxide produced by light absorption may either fluoresce by dropping back to lower energy levels or, on collision with other molecules, enter into chemical reaction or lose its excitation energy in other ways such as degradation to heat motion. These considerations lead to the expression[8]

$$\frac{I}{I_0} = \frac{1}{\frac{\tau}{t} + 1} = \frac{1}{ap_{NO_2} + 1} \tag{1}$$

I_0 is the intensity of the fluorescence at zero pressure, I, the intensity at the pressure p_{NO_2} and τ the natural life of the excited molecule before dropping back to a lower level. The mean time between collisions, t, is inversely proportional to the pressure and from kinetic theory has the value

[8] Stern and Volmer, *Physik. Z.*, **20**, 183 (1919).

$$t = \frac{1}{N\sigma_{12}^2(8\pi kT)^{1/2}\left(\frac{m_1 + m_2}{m_1m_2}\right)^{1/2}} \qquad (2)$$

At 25° this reduces to the numerical form

$$t = \frac{3.90 \times 10^{-23}}{p\left(\frac{M_1 + M_2}{M_1M_2}\right)^{1/2}} \qquad (3)$$

with the pressure, p, in mm. of mercury. Any efficiency factor may be included in σ_{12}, the distance between nuclei for a quenching collision. The constant a in Equation 1 is an abbreviation

$$a = 2.56 \times 10^{22}\left(\frac{M_1 + M_2}{M_1M_2}\right)^{1/2}\sigma_{12}^2\,\tau \qquad (4)$$

A plot of $1/I$ against the pressure gives a straight line with the slope a/I and intercepts $1/I_0$. Run 1 when treated in this manner gives $a = 50$ mm.$^{-1}$. Run 2 similarly results in $a = 47$. These results were checked in the following manner. Values of I_0 were calculated from Equation 1 for each observed point with assumed values of the constant a. With the correct a the set of values of I_0 so obtained should be constant over the whole range. In this manner a was found to be equal to 50 mm.$^{-1}$ for Run 1 and between 45 and 50 mm.$^{-1}$ for Run 2. One run with illumination by λ4047 alone leads to $a = 40$. This latter value is necessarily approximate, due to the difficulties attending the measurement of the feeble intensity of fluoresced light in this case. In the sixth column of Table I are given the values of I calculated from the expression

$$\frac{I}{I_0} = \frac{1}{50p_{NO_2} + 1}$$

with $I_0 = 8.3$ in Run 1 and 5.9 in Run 2. Inspection of the last two columns of the table shows that the functional relationship between the pressure of nitrogen dioxide and the intensity of fluorescence given by Equation 1 holds quantitatively over a pressure range of 12,000-fold with a corresponding variation in the intensity of 850-fold. Such agreement is confirmation of the general idea that the light first produces an excited molecule which may then fluoresce or be damped by collision.

It is evident that at a pressure of nitrogen dioxide of 0.02 mm. the fluorescence is half damped. From the experimental result $a = 50 = 5.35 \times 10^{21}\sigma_{12}^2\tau$ it follows that $\sigma_{12}^2\tau = 9.3 \times 10^{-21}$ cm.^{2} sec. If we assume τ is 10^{-7} sec., σ_{12} must be 30×10^{-8} cm. or about ten times ordinary kinetic theory diameters. On the other hand, if σ_{12} is taken equal to 3×10^{-8} cm., τ must be as long as 10^{-5} second. The lives of excited atoms, investigated by Wien[9] and Kerschbaum,[10] are all of the order of magnitude of 10^{-7} or 10^{-8} seconds. It is natural to suppose that the lives of optically

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[9] Wien, *Ann. Physik*, **83**, 1 (1927).

[10] Kerschbaum, *ibid.*, **83**, 287 (1927).

excited molecules should be of the same order of magnitude. On the other hand, it is quite common for large diameters to appear in collisions of the second kind. For example, the measurements of Stuart[11] on the quenching of the resonance fluorescence of mercury by hydrogen and carbon monoxide lead to diameters of the excited mercury atom several times that of the normal atom. Also Mannkoff[12] finds similar dimensions in the case of damping of fluorescence in sodium vapor by nitrogen and hydrogen. Kallmann and London[13] have treated on a quantum mechanical basis the problem of abnormally large effective diameters and succeeded in giving a reasonable explanation of their repeated appearance in terms, among other things, of the closeness of resonance between the two systems. Thus, depolarization by sodium vapor of the fluorescence of the D-lines of sodium[14] may occur at distances many thousand-fold ordinary kinetic theory values. Hence we may conclude that the apparently large diameters found here in the quenching of the nitrogen dioxide fluorescence by nitrogen dioxide itself are reasonable and that there is no necessity for assigning an exceptionally long life (10^{-5} second) to the optically excited nitrogen dioxide molecule.

Quenching of Fluorescence by Foreign Gases.—The addition of oxygen, hydrogen, nitrogen or carbon dioxide to the nitrogen dioxide produces a noticeable decrease in the intensity of the fluorescence. Figure 1 illustrates the quenching of the nitrogen dioxide fluorescence in the presence of oxygen. Such an effect is to be expected since in this case more collisions of the second kind should occur. In place of Equation 1 we have

$$\frac{I}{I_0} = \frac{1}{\Sigma_i \frac{\tau}{t_i} + 1} \tag{5}$$

When there is only one added gas this becomes, using the experimental result of the preceding section

$$\frac{I}{I_0} = \frac{1}{50p_{NO_2} + ap + 1} \tag{6}$$

Calling J_0 the observed intensity in pure nitrogen dioxide at the pressure p_{NO_2}, and J the intensity after the addition of the pressure, p, of foreign gas we obtain the ratio

$$\frac{J}{J_0} = \frac{p_{NO_2}\,(I)_{p=p}}{p_{NO_2}\,(I)_{p=0}} = \frac{50p_{NO_2} + 1}{50p_{NO_2} + ap + 1} = \frac{1}{cp + 1} \tag{7}$$

where $c = a/(50p_{NO_2} + 1)$, a constant for any particular pressure of nitrogen dioxide.

Table II contains the experimental results on the quenching of the fluorescence by various gases. The observations are given in full for the

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[11] Stuart, *Z. Physik*, **32**, 262 (1925); Gaviola, *Phys. Rev.*, **33**, 309 (1929).

[12] Mannkoff, *Z. Physik*, **36**, 315 (1926).

[13] Kallmann and London, *Z. physik. Chem.*, **2B**, 207 (1929).

[14] Datta, *Z. Physik*, **37**, 625 (1926); Hanle, *ibid.*, **41**, 164 (1927).

case of nitrogen; the other gases give similar results. The values of c are indeed constant within the experimental error throughout any single run. Moreover, the values of a calculated from each run are in good accord among themselves, as seen from the last column of Table II, thus establishing the general validity of Equation 6, which relates the intensity of fluorescence to the pressure of both nitrogen dioxide itself and the foreign gas. The effect of nitrogen tetroxide has been neglected. In the preceding section this factor comes into question only at the highest pressures, where the observations may already be in error in the correction for light transmission. Since, however, carbon dioxide is practically as efficient in quenching as nitrogen dioxide, we might assume that nitrogen tetroxide has also the same efficiency. The pressure p_{NO_2} should then be replaced by $p_{NO_2} + p_{N_2O_4}$. This would lead to a somewhat better check among the various values of a.

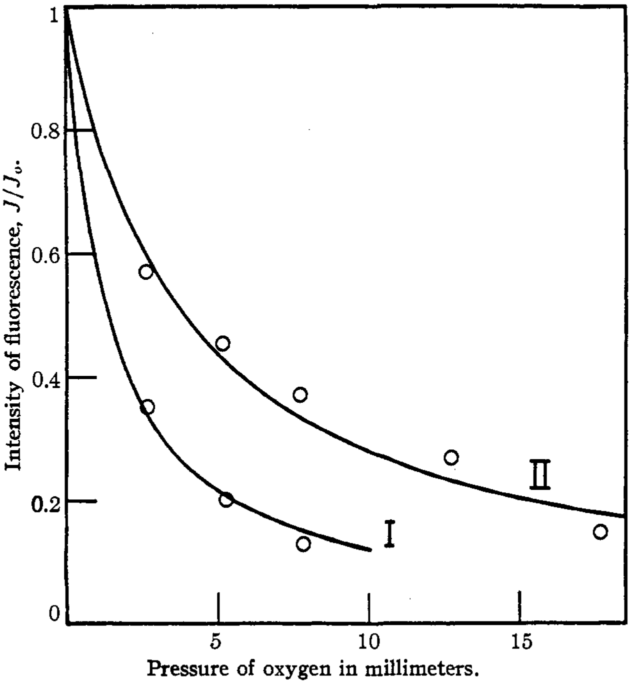

Fig. 1.—Quenching of fluorescence by oxygen. Solid curve from $\frac{J}{J_0} = \frac{1}{\frac{16.5}{50P_{NO_2} + 1}P_{O_2} + 1}$. I, P_{NO_2}, 0.436 mm.; II, P_{NO_2}, 1.256 mm.

It is to be noticed that the pressure of added gas which damps the fluorescence to one-half is not an immediate measure of the life of excited

TABLE II

QUENCHING OF FLUORESCENCE BY FOREIGN GASES

Added gas	p_{NO_2}, mm.	$p_{N_2O_4}$, mm.	$p_{\text{added gas}}$, mm.	J/J_0	c, mm.$^{-1}$	a, mm.$^{-1}$
Nitrogen	0.587	0.005	2.62	0.384	0.61	
			5.21	.191	.81	
				Average	0.71	22
	1.685	0.038	2.60	0.566	0.29	
			5.17	.465	.22	
			7.70	.388	.20	
			10.2	.334	.20	
			12.7	.257	.23	
			15.2	.193	.27	
				Average	0.237	20
Hydrogen	0.378	0.002	2.62	0.211	1.43	28
	1.085	.018			0.44	24
				Average		26
Oxygen	0.436	.002			0.75	17
	1.256	.017			0.25	16
				Average		16.5
Carbon dioxide	0.857	.006			1.15	50
	.940	.010			0.98	47
	2.18	.047			.35	37
				Average		44

nitrogen dioxide and the deactivating diameter, since the ratio of observed intensities is a function also of the pressure of nitrogen dioxide. Rather the value of a is such a measure; its reciprocal gives the pressure at which the fluorescence would be half damped if there were no quenching by nitrogen dioxide itself. Table III contains a summary of the experimental results. The product, $\sigma_{12}^2\tau$, was calculated from a by means of Equation 4. Column 5 contains the relative efficiencies of the various added gases in quenching fluorescence, nitrogen dioxide arbitrarily being set equal to unity. The last column gives the value σ_{12}, the effective deactivational diameter, assuming a mean life of the excited nitrogen dioxide molecule of 10^{-7} second.

The specific nature of collisions of the second kind is shown by Table III. Carbon dioxide is practically as effective as nitrogen dioxide in quenching, while nitrogen, oxygen and hydrogen are only one-quarter or one-fifth as effective in this respect. The molecular complexity of the triatomic molecules, CO_2 and NO_2, implies a greater number of higher energy levels than is possessed by the simpler diatomic molecules. It is known that collisions of the second kind are more effective for those cases in which a small amount only of the excitation energy is to be transformed into kinetic energy. It is therefore not surprising that carbon dioxide and nitrogen dioxide are indeed the more efficient in damping fluorescence.

Table III

Efficiency of Quenching Collisions

Quenching gas	a, mm.$^{-1}$	$p^{1}/_{2}$, mm.	$\sigma_{12}^2\tau \times 10^{21}$ cm.^{2} sec.	Relative efficiency	$\sigma_{12} \times 10^8$ ($\tau = 10^{-7}$ sec.), cm.
NO_2	50	0.020	9.3	1	31
CO_2	44	.023	8.2	0.87	29
N_2	21	.048	2.7	.29	16
O_2	16.5	.061	2.2	.24	15
H_2	26	.038	1.4	.15	12

Summary

The intensity of fluorescence excited in nitrogen dioxide by the 4358 and 4047 Å. lines of the mercury arc has been determined for the pressure range 0.001 to 18 mm. Nitrogen dioxide is very efficient as a quenching agent; the fluorescence is half damped at a pressure of 0.02 mm. The product of the square of the effective diameter for collision and the life of the excited molecule $\sigma_{12}^2\tau$ is 9.3×10^{-21} cm.^{2} sec. This result indicates a deactivational diameter approximately ten times greater than kinetic theory values.

It is shown that the quenching of this fluorescence by foreign gases is in quantitative agreement with Equation 7, which is based on the occurrence of deactivating collisions with these gases as well as with nitrogen dioxide itself. There is specificity in quenching by added gases; the relative deactivational efficiencies of carbon dioxide, nitrogen, oxygen and hydrogen referred to nitrogen dioxide as unity are, respectively, 0.87, 0.29, 0.24 and 0.15.

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[Contribution from the Chemical Laboratory of the University of Saskatchewan, Saskatoon, Saskatchewan]

STUDIES ON THE THERMOCHEMISTRY OF THE COMPOUNDS OCCURRING IN THE SYSTEM $CaO-Al_2O_3-SiO_2$. IV. THE HEAT OF SOLUTION OF TRICALCIUM ALUMINATE AND ITS HYDRATES IN HYDROCHLORIC ACID[1]

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The heats of solution of the compounds occurring in the system $CaO-Al_2O_3-SiO_2$ and of their hydration products are of interest not only for the purpose of calculating the heat of formation of these compounds but also in connection with problems relating to the constitution of hydraulic cements and elucidation of the reactions which take place during their hydration. This applies especially to the aluminates and the silicates of calcium which are rich in lime. The paucity of such data is probably mainly due to the difficulty of preparing sufficient quantities of these substances in a pure

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