The great energy efficiency indicates that it is a chain reaction. The denominators of the above equations are similar to those found by Bäckström[3] to express the negative catalysis of alcohols in the oxidation of sodium sulfite which is a chain reaction. The effect of oxygen and ferric chloride can best be explained by Bäckström's theory that the effect of the negative catalyst is to break the chains.

It seems probable that the primary step is the decomposition of the complex according to this equation

$$HgCl_2C_2O_4^{=} + \text{energy} = HgCl + Cl^- + C_2O_4^-$$

The half-oxidized oxalate, $C_2O_4^-$, would then reduce the $HgCl_4$ in another $HgCl_2C_2O_4^{=}$ and the energy of reaction may cause the oxalate ion in the complex to decompose, giving products which may react in the same way as the half-oxidized oxalate. These chains would end if the intermediate products were oxidized by either oxygen or ferric chloride. Such a mechanism is in agreement with the above experimental equation for the rate of reaction.

The observed temperature coefficient will be the sum of the temperature coefficients for the reaction and for the dissociation of the complex ions.

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A METHOD FOR DETERMINING THE VISCOSITY OF CORROSIVE GASES AND THE MOLECULAR DIAMETER OF NITROGEN PENTOXIDE

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Introduction

The decomposition of nitrogen pentoxide has been much studied during the past few years in connection with the subject of reaction rates as it is one of the few, and of these the oldest of, unimolecular reactions. In papers dealing with the kinetics of the nitrogen pentoxide reaction, it has ordinarily been assumed to have a molecular diameter of 10^{-7} cm. Recent calculations by Tolman, Yost and Dickinson[1] and by Lewis[2] show that in order for it to be activated sufficiently rapidly it should have the extraordinarily large diameter of 6.07×10^{-6} cm. In this case one of the molecules is activated, which may greatly modify its effective diameter. It seems of interest, however, to determine this value by viscosity measurements.

[3] H. N. Alyea and H. L. J. Bäckström, THIS JOURNAL, 51, 90 (1929).

[1] Tolman, Yost and Dickinson, *Proc. Nat. Acad. Sci.*, 13, 188 (1927).

[2] Bernard Lewis, *Science*, 66, 331 (1927).

Experimental

A diagram of the apparatus is shown in Fig. 1. It was made entirely of pyrex glass without stopcocks. The nitrogen pentoxide at a pressure of 51 mm., in A, passed through the capillary D and was condensed by liquid air in the U-tube E. Nitrogen pentoxide was introduced into A, before beginning the measurements, by vacuum distillation from a mixture of white fuming nitric acid and phosphorus pentoxide, contained in a glass vessel sealed to B. The nitrogen pentoxide in some experiments was condensed in A by liquid air, in others by a mixture of ice and brine. During the distillation a low pressure was maintained by pumps at both J and H. After sufficient nitrogen pentoxide had accumulated in A, the arm B was sealed off, the cooling bath removed from A and evacuation at J continued until the nitrogen pentoxide crystals were colorless. The cooling bath was then applied to A and the arm J sealed off. The cooling bath at A was now replaced by a large Dewar containing clean ice, which maintained a temperature of 0° to within 0.1° throughout the remainder of the experiment. A water pump circulated water from a refrigerator through the cooling jacket C. A thermometer showed this temperature to be constant at 4° to within less than 0.5° during all experiments. The cooling jacket was wrapped with asbestos. The low temperature prevented decomposition of the nitrogen pentoxide while passing through the capillary.

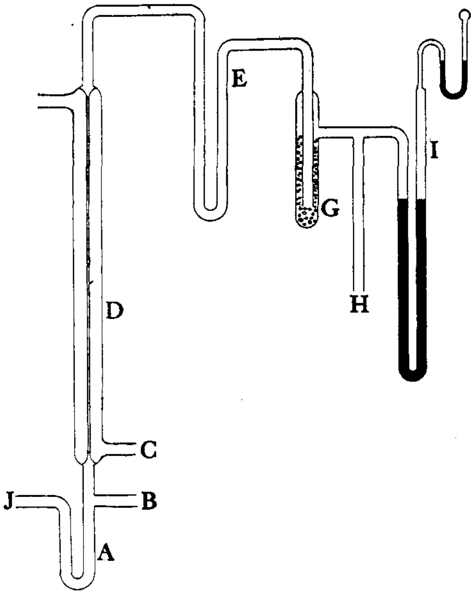

Fig. 1.—Apparatus for measuring the viscosity of a corrosive gas.

After the nitrogen pentoxide had been passing through the capillary and into the soda lime at G for from two to three hours, liquid air was applied to the U-tube at E and the time accurately noted. The high vacuum pump at H maintained a vacuum better than 0.1 mm. at all times, as shown by the mercury gage I. After nitrogen pentoxide had been condensing in E for two hours the two arms of the U-tube were sealed off at E. The exact time the left arm was sealed off was noted.

The sealed U-tube containing the nitrogen pentoxide was broken beneath the surface of standardized sodium hydroxide by pushing the two arms together. The sodium hydroxide filled the two evacuated arms, reacting with the nitrogen pentoxide without loss. The two arms were then carefully washed and the sodium hydroxide back-titrated with hydrochloric acid.

The variation of 0.1° in the ice-bath A results in a change in the vapor pressure of 0.5 mm. in a total pressure of 51 mm.[3] The amount of nitrogen pentoxide collected in unit time did not vary with a many-fold change in the surface of nitrogen pentoxide, proving that the pressure of nitrogen pentoxide in A did not lag appreciably behind the equilibrium pressure during the experiments.

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[3] Daniels and Bright, This Journal, **42**, 1131 (1920).

The capillary was standardized by passing definite volumes of nitrogen and oxygen through the apparatus under a small constant pressure. The pressure was maintained by a short column of mercury with gas on both ends held together by surface tension. The method is described by A. O. Rankine.[4] The modification used is here described. To the U-tube A a three-way stopcock was connected. One of the arms of the stopcock connected with a flask containing the purified gas. The remaining arm connected with a 6-mm. glass tube of the same length as the capillary and parallel to it. This tube was cooled by a cold water jacket in series with the cooling jacket C. Inside this tube was a column of mercury about 2 cm. long which descended in the tube as the gas escaped through the capillary D. This maintained a constant pressure on the escaping gas, depending only on the length of the column since the tube was open to the atmosphere above the column and also at the tube H. The mercury column moved between two lines on the tube, thus always expelling a known volume of gas, and the corresponding time was noted. It could be forced back up the tube for another experiment by turning the three-way stopcock to connect the tube with the flask and then carefully manipulating the adjustable manometer. The cross sectional area of the tube containing the mercury column was determined by measuring its length and then weighing it. The tube was of very uniform bore between the marks, which were a meter apart. The volume between the marks was found to be 7.63 cc. After each series of experiments the column was forced up into a short auxiliary tube which could then be removed and weighed.

Results

In the calibration experiments the pressures on the capillary were 740 mm. plus the pressure of the mercury column on one end and 740 mm. on the other. The gases used were air and oxygen and in each experiment the time t_1 taken for the mercury column to move through one meter, expelling 7.63 cc. at 4°, was noted. From the data one can calculate what volume of air and oxygen, respectively, would be expelled in the time t_1 if the pressure on one end of the capillary were 51 mm. and on the other approximately zero, as in the nitrogen pentoxide experiment. Poiseuille's equation may be written

$$\frac{V}{t} = \frac{\pi r^4}{8\eta}\frac{\mathrm{d}p}{\mathrm{d}x} \tag{1}$$

where t is the time, r is the radius of the capillary, η is the viscosity and V is the volume of gas which passes at the point where the rate of change of pressure with distance is $\mathrm{d}p/\mathrm{d}x$. Using the gas law we have $V = nRT/p = k/p$; making this substitution for V in (1) and integrating, we obtain $p^2 = 16\eta kx/\pi r^4 t$, providing we suppose p to be zero when $x = 0$.

Thus if a capillary of uniform bore is considered in which the pressure at one end is zero and at the other $740 + a$, the ratio of the lengths of the segments L_1 in which the pressure drops from $740 + a$ to 740 mm. to the segment L_2 in which it drops from 51 to zero is

$$\frac{L_1}{L_2} = \frac{(740 + a)^2 - 740^2}{51^2} = a\left(\frac{1480 + a}{51^2}\right)$$

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[4] A. O. Rankine, *Proc. Roy. Soc.* (London), **83**, 516 (1910).

The same number of molecules would stream through these two segments in equal time. For two segments of the same length with the respective pressure drops 740 + a to 740 mm. and a second of 51 to zero mm., the number of molecules N_1 and N_2 emitted in equal times will be in the ratio

$$\frac{N_1}{N_2} = \frac{L_1}{L_2} = a\left(\frac{1480 + a}{51^2}\right)$$

and

$$\frac{V_1}{V_2} = a\,\frac{(1480 + a)}{51^2} \times \frac{15}{(740 + a)}$$

where V_1 and V_2 are the volumes passing through in the time $t_1 = t_2$. Here the volumes are measured at the high pressure ends of the capillary. In every case, V_1 was 7.63 cc. If V_3 is the volume of nitrogen pentoxide which streams through the same capillary in time t_3 when the pressure on one end is 51 mm. and zero on the other, we write

$$\frac{\eta_3}{\eta_1} = \frac{V_2/t_2}{V_3/t_3} = \frac{V_1 t_3}{V_3 t_1}\,\frac{(740 + a)}{(1480 + a)}\,\frac{51}{a}$$

where η_3 is the viscosity of nitrogen pentoxide and η_1 is the viscosity of air or oxygen.

Any two molecular diameters σ_1 and σ_3 are in the ratio $\sigma_3/\sigma_1 = M_3^{1/4}\eta_1^{1/2}/M_1^{1/4}\eta_3^{1/4}$, where M_1 and M_3 are the corresponding molecular weights. Thus

$$\sigma_3 = M_3^{1/4}\sqrt{\frac{V_3}{t_3}}\left(\frac{\sigma_1}{M_1^{1/4}}\right)\sqrt{\frac{t_1(1480 + a)a}{V_1(740 + a)51}}$$

The following table gives the data for the calibration runs.

TABLE I

EXPERIMENTAL CALCULATION

Gas	V_1	t_1	a	b	$c \times 10^{-8}$
Air	7.63	379.8	17.63	0.1719	7.81
Air	7.63	337.4	19.88	.1715	7.82
Air	7.63	343.2	19.65	.1713	7.83
O_2	7.63	340.9	22.25	.1613	7.72
O_2	7.63	198.3	37.78	.1630	7.63
O_2	7.63	339.3	22.50	.1611	7.73
O_2	7.63	211.5	33.90	.1668	7.49
			Average		7.72

In the table, V_1 is in cc., t_1 in seconds and a in mm. and $b = \sqrt{\frac{t_1}{V_1}\,\frac{(1480 + a)a}{(740 + a)51}}$ and $c = \frac{\sigma_1}{M_1^{1/4}}\,b$. For oxygen σ_1 is taken equal to 2.96×10^{-8} and for air 3.10×10^{-8}. The other quantities have been defined.

Nitrogen pentoxide was permitted to run for 7200 seconds in five experiments, giving volumes V_3 of nitrogen pentoxide calculated to 51 mm. and 4° shown in Table II.

TABLE II

RESULTS OF EXPERIMENTS

Gas	V_3	$\sqrt{V_3/t_3}$	$\sigma_3 \times 10^8$
Nitrogen pentoxide	805	0.334	8.33
Nitrogen pentoxide	793	.332	8.26
Nitrogen pentoxide	905	.354	8.80
Nitrogen pentoxide	916	.356	8.67
Nitrogen pentoxide	804	.336	8.33
		Average	8.53

Thus the average value for the molecular diameter of nitrogen pentoxide is 8.53×10^{-8}.

Discussion of Possible Errors

When a column of mercury descends in a tube it encounters a viscous resistance which might appreciably reduce the pressure on the gas escaping through the capillary. A simple calculation shows that this was not the case in the above calibration. In a typical experiment the length of the mercury column was 1.79 cm. and its radius was 0.1537 cm. The volume swept out was 7.63 cc., the time 379.8 sec.; the viscosity of mercury at 20° is 0.01589. Substitution of these values in Poiseuille's equation gives a viscous resisting pressure due to the descent of the mercury column itself of 24.8 dynes. This is to be deducted from the pressure due to the mercury column, which is 23,800 dynes. The viscous resistance is thus negligible.

In the experiment with nitrogen pentoxide the pressure at the end of the capillary next to the liquid air was low. The kinetic theory for viscosity applies only for pressures such that the mean free path is small compared with the diameter of the capillary. From the rate with which air flowed through the capillary its mean diameter was found to be 0.0294 cm. The molecular diameter is found to be 8.53×10^{-8} cm., so that the nitrogen pentoxide molecules will have a mean free path of 0.029 cm. at a pressure of 0.04 mm. Even if the resistance to flow should drop to zero for the last 0.04 mm. of the 51-mm. pressure drop or rise to ten times the value from the kinetic theory, this error should be small. Actually, a pressure of nitrogen pentoxide as low as 0.04 mm. was never reached since the space E was evacuated only by a Hyvac pump and the pressure of permanent gas as shown by the manometer I was only kept less than 0.1 mm. This small residual pressure also lessened any chance of distillation of nitrogen pentoxide from E to G. Actually, all the nitrogen pentoxide was observed to condense on the first centimeter or two submerged in liquid air, leaving a path about ten time as long through the cooled tube on which there was no visible condensate.

The gas emerges from the capillary with an axial velocity. Thus a part of the pressure drop is not used in overcoming viscous resistance. In the calibration experiments, since the increase in volume, and therefore velocity, is less than in the nitrogen pentoxide experiments, it will be sufficient to show that for nitrogen pentoxide the energy used in communicating velocity is only a small fraction of that used in overcoming viscous resistance. If the pressure at the low pressure end be taken as 0.1 mm., the velocity will be such as to use up less than 0.3% of the 51-mm. pressure drop. This figure is an upper limit to this error.

Conclusions

An experimental arrangement for measuring viscosities of corrosive gases is described.

The molecular diameter of nitrogen pentoxide is found to be 8.53×10^{-8} cm.

[Contribution from the Analytical Laboratory of the State University of Iowa]

OXIDATION-REDUCTION POTENTIALS. II. THE MANGANESE DIOXIDE ELECTRODES

By Stephen Popoff, J. A. Riddick and W. W. Becker

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The standard oxidation–reduction potential of the permanganate–hydrogen–manganous ion electrode is of considerable importance both from the point of view of reliable electromotive force constants and from its use in making suitable predictions. Since it is not possible to measure directly the foregoing potential, one must resort to calculations involving electromotive force measurements of the cells

$$\mathrm{Pt} \mid \mathrm{H_2, H^+} \mid \mathrm{H^+ + MnO_4^- + MnO_2} \mid \mathrm{Pt}, \text{ and} \qquad (A)$$

$$\mathrm{Pt} \mid \mathrm{H_2, H^+} \mid \mathrm{H^+ + Mn^{++} + MnO_2} \mid \mathrm{Pt} \qquad (B)$$

If E_A and E_B represent the standard oxidation–reduction potentials of Cells A and B, respectively, then the standard oxidation–reduction potential (E_C) of the cell

$$\mathrm{Pt} \mid \mathrm{H_2, H^+} \mid \mathrm{H^+ + Mn^{++} + MnO_4^-} \mid \mathrm{Pt} \qquad (C)$$

can be calculated from the equation $(3E_A + 2E_B)/5 = E_C$. This calculation was made using the value of E_A obtained by Brown and Tefft,[1] and the value of E_B obtained by Tower.[2] It was noted, however, that Brown and Tefft employed chemically prepared manganese dioxide which analyzed over 99%, while Tower employed electrolytically prepared manganese dioxide whose analysis was not given. It was further observed that the potentials with electrolytic manganese dioxide varied according to the current density employed in its preparation and that the values in the literature for the potential of the manganese dioxide–permanganate electrode differed by more than 0.1 volt.

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[1] Brown and Tefft, This Journal, **48**, 1128 (1926).

[2] Tower, *Z. physik. Chem.*, **32**, 566 (1900).